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A SEARCH FOR CARBON AND ITS COMPOUNDS IN LUNAR SAMPLES FROM MARE TRANQUILLITATIS

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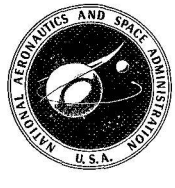

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INTRODUCTION

This report assembles information obtained during a comprehensive organic analysis of lunar materials from Mare Tranquillitatis by a consortium of investigators at Ames Research Center. The samples studies were obtained during the Apollo 11 mission, and were distributed to the scientific community by the Lunar Receiving Laboratory. On October 6, 1969, this comprehensive analysis began on Sample 10086 Bulk A Fines, comprising 100.5 g of fine-grained (<1 mm) black lunar fines.

Knowledge of the chemical state of carbon in lunar materials is important in understanding the cosmological history of carbon and in providing new data points for our studies of chemical evolution and the origin of life. Apollo 11 provided, for the first time, samples that are not a part of our terrestrial system and have not been exposed for extended periods of time to the earth's biosphere.

The analytical scheme that guided the analysis, shown in figure 1, was designed to obtain maximum information from samples that contain minimal concentration of carbon or carbon-containing compounds. Preliminary examinations of lunar samples (ref. 1) suggested that the concentration of carbon to be expected in these samples would be very low, in the order of about 10 μg/g or less. The analysis method follows generally accepted organic geochemical practices but its application to a single sample is unique. Before analysis of the lunar sample, this scheme of analysis was tested on a modern sediment from Saanich Inlet, British Columbia; a basalt bomb from Hawaii; and the Pueblito de Allende meteorite from Mexico.

A portion of the fine-grained material was divided into seven parts, the weights of which were determined by the nature of the experiment. After a complete pass through the analytical scheme, the analyses providing the greatest information were repeated on additional aliquots of the sample. Table 1 shows the total weights of samples provided for the various experiments shown in the scheme.

Part I

BULK LUNAR SAMPLE

1. MASS SPECTROMETRY ANALYSIS *Allen Duffield and Don Ramey*

METHOD

This experiment was designed to determine the presence and structure of volatile organic material that would be ionized directly in the source of a CEC 110 high-resolution mass spectrometer (MS) at temperatures ranging from 80° to 300° C.

A background blank for the MS was determined on a photoplate, and this background was used in the interpretation of photoplates obtained during the low-temperature pyrolysis of the lunar sample.

A 7-mg portion (essentially the maximum allowable quantity) was introduced into the MS, and 11 photoplate exposures were taken while the temperature of the ion source was increased from 80° to 300° C.

RESULTS

1. No significant increase in hydrocarbon fragments above the blank reading could be discerned. Note that 1 ppm of 7 mg (the sample quantity used) = 7×10^{-9} g. Instrument sensitivity with sample introduction by the probe is $\sim 10 \times 10^{-9}$ g per compound.
2. The series of ions shown in table 2 were marginally above the background level. It appears more than a coincidence that most of the ions contain nitrogen, but any assignment to definite organic structures would be speculation.

This work was repeated. The sample was heated to 300° C and one photoplate exposure was taken over a period of 7 min. Results were:

1. A large amount of di-*n*-octylphthalate (a constituent of diffusion pump oil) was identified. This material was absent in the background exposure plate.
2. Ions formally corresponding to formic acid, acetic acid, and sulfur dioxide were found, as well as a series of oxygen-containing ions.
3. The nitrogen-containing fragments observed in the first sample could not be reproduced.

INTERPRETATION

1. Di-*n*-octylphthalate represents a contaminant of unknown source in the lunar sample.
2. The lack of reproducibility of nitrogen-containing fragments indicates that wherever found they must be ascribed to instrument background.
3. Significance of the oxygen fragments is not immediately apparent.

2. ORGANIC CARBON *Richard Johnson and Catherine Davis*

Volatile carbon-hydrogen compounds that burn in a hydrogen flame were measured in about 30 mg of the lunar sample. The sample was pyrolyzed at 800° C under hydrogen and helium, and the resulting volatile products were swept directly into a hydrogen flame-ionization detector. The resulting single-peak area was compared with that from calibrated standards, corrected for the background blank, and converted into organic concentrations in parts per million. Table 3 compares the results obtained from sand blanks, the Pueblito de Allende meteorite sample, and the lunar sample.

RESULTS

The concentration of organic carbon as determined by this method is about 40 μg/g. Preliminary examination of a number of lunar samples by the same technique showed that the amount of indigenous carbon in Apollo 11 samples generally was less than about 10 μg/g after corrections were made for possible contamination.

INTERPRETATION

The exact nature of this carbon cannot be determined on the basis of this experiment alone. Later it will be shown that some of this material may have been accounted for in the 1N HCl hydrolysate as polyorganosiloxanes.

3. CARBON *Sherwood Chang, John W. Smith, Jim Lawless, and Ian Kaplan*

The lunar sample was studied for total carbon content and to identify some types of nonextractable and volatile carbon compounds. Products derived from a variety of experiments involving pyrolysis and acid treatment of the sample have been examined.

EXPERIMENTAL

Prior to analysis, all lunar samples were degassed by heating at 150° C at 10^{-3} torr for 48 hr. Evolved condensable gases were collected in a sampling bulb immersed in liquid nitrogen. Gas chromatography (GC) of the bulb contents showed the presence of trace C_2, C_3, and C_4 hydrocarbons. $\delta^{13}C$ ratios of total carbon (ref. 2) have clearly demonstrated the need for removal of possible volatile contaminants in this manner.

Total Carbon

Total carbon was measured by combustion of 1-g samples in an oxygen atmosphere at about 700 mm Hg at 1050° C. The gaseous products were passed over copper oxide catalyst, silver wire, and lead oxide (to remove halogens and oxides of nitrogen and sulfur, respectively). The resulting CO_2 was purified from water by distillation through a dry-ice/acetone trap and its volume measured on a manometer. Details of the combustion apparatus are given in reference 3.

Volatile Carbon Compounds

Acid treatment. Estimations of the concentration of carbide carbon in samples of lunar fines, the Mighei carbonaceous chondrite, and cohenite (Fe_3C, removed from Canyon Diablo iron

meteorite) were obtained from analysis of gaseous hydrolysis products generated by the procedure outlined below.

A reaction tube, sealed at one end with a breakable glass diaphragm, was cooled to −120° C in a bath of isohexane-liquid nitrogen, and 3 ml of 4.8N hydrochloric acid was added. When the acid had frozen, the weighed, powdered sample was introduced; and the reaction tube, still at a temperature of −120° C, was connected to a vacuum system. Entrapped air was exhausted from the tube as quickly as possible to a pressure of less than 10^{-2} torr, and the tube was sealed with a flame. After shaking to thoroughly mix the contents, the tube was heated at 98° C for 16 hr. The tube was cooled and reconnected to the evacuated system, and the gas-retaining seal was fractured with an externally controlled iron rod. The gas evolved from the Mighei chondrite was collected directly at −195° C in a tube containing about 100 mg freshly activated charcoal, sealed at one end with a breakable glass diaphragm. The gases from the lunar fines and cohenite, however, were held over outgassed, concentrated solutions of either zinc sulfate or potassium hydroxide to remove hydrogen sulfide or a mixture of hydrogen sulfide and carbon dioxide, respectively, prior to their final collection. Noncondensable gases were present in every experiment and could not be collected quantitatively. The gas sample tubes were flame sealed when the pressure in the system had fallen to a constant minimum.

The residue from hydrochloric acid hydrolysis of the lunar fines was extracted with boiling benzene. The extract was evaporated almost to dryness and examined by GC.

During analysis for sulfur (ref. 2), other lunar materials (10002,54, breccia; 10049, hard rock; 10057,40, hard rock; 10060,22, breccia; 10084, fines) were warmed to 60° C in 85% phosphoric acid and allowed to stand overnight at 25° C. Gases not trapped in 5% silver nitrate solutions were collected at −195° C over freshly activated charcoal and preserved for analysis.

Estimates of the concentration of carbon monoxide, carbon dioxide, and other volatile compounds freed during digestion of the lunar sample with hydrofluoric acid (HF) treatment were obtained by analysis of the gaseous products. The reaction was carried out in a teflon-lined tube, and the mixture was stirred with a teflon-coated magnet for 18 hr at 25° C. Evolved gases were collected at −195° C on 5Å molecular sieves freshly activated at 400° C and 10^{-3} torr. Otherwise, the procedure used was essentially that described for hydrolysis of carbides. In all cases, gas collection methods and reagents were monitored by parallel control experiments.

Residues from repeated treatment of lunar fines with hydrochloric and hydrofluoric acid were combusted in oxygen as described above and the total residual carbon determined as carbon dioxide.

Pyrolysis

The simple pyrolysis system shown in figure 2 was connected to the combustion apparatus (ref. 3). The stored sample was again outgassed at 150° C (for 2 hr) under vacuum and a 1-g sample was pyrolyzed under vacuum over three temperature ranges: 150°–250° C, 250°–500° C, and 500°–750° C. The volatile products released were frozen into a sampling bulb immersed in liquid nitrogen, the products from each pyrolysis step being condensed directly into separate sample bulbs. The contents of these bulbs were reserved for analysis by GC and MS. The total quantity of carbon remaining in the final pyrolysis residue was determined by measuring the carbon dioxide produced on combustion at 1050° C.

In a separate experiment, after completion of pyrolysis at 750° C, the pyrolysis chamber was evacuated and cooled to 25° C. It was then filled to 76 torr with a 1:4 mixture of carbon monoxide and hydrogen. Products obtained by reheating at 750° C for 1 hr were collected in the usual fashion.

Methods of Analysis

High- and low-resolution mass spectra were obtained with CEC 21-110 and 21-491 mass spectrometers, respectively, at an ionizing voltage of 70 eV. Quantitation on the 21-110 was accomplished by comparing the abundances of characteristic ions in sample spectra with those of corresponding ions in spectra of known amounts of reference compounds. The detectable concentration limit of a single compound was about 8 μg for each gram of lunar fines.

GC analyses for hydrocarbons were conducted on two instruments equipped with single-flame ionization detectors (Varian Aerograph Models 1520B and 200B). The 1520B was operated in the dual-column, thermal-conductivity mode for detection of carbon dioxide. All analyses of material with molecular weight less than 75 were performed on a 6-ft X 0.125-in. stainless steel column packed with 100–120 mesh Poropak Q. For higher molecular weight material, a 5-ft X 0.125-in. stainless steel column packed with 3% SE-30 on 100–120 mesh Gaschrom Z was used.

Gas sample tubes were fitted with ground-glass vacuum stopcocks and evacuated to 10^{-6} torr before the gas-retaining seals were broken. Prior to GC, the end of the stopcock was sealed with a silicone rubber septum and evacuated through a syringe needle. The tubes were heated to 200° C for 10 min, and sampling was conducted through the septum with a gas-tight Hamilton syringe. Since sample tubes were usually at reduced pressure, the syringe always was partially filled with laboratory air prior to insertion in the injection port. When appropriate, corrections were made for possible atmospheric contamination. In the carbon dioxide determination, the large uncertainties involved made the results only qualitatively useful. Methane was present in laboratory air, but only in barely detectable amounts. Quantitation was based on detector responses to known volumes of standard gases. Using gas-tight syringes, injections were routinely reproducible to ±10%. A detection limit could be set at 4 X 10^{-3} μg of any C_1 to C_4 hydrocarbon per gram of sample.

RESULTS AND DISCUSSION

Total Carbon

The average total carbon concentration in duplicate analyses of 10086,3 Bulk A lunar fines was 157 ± 14 μg/g. In good agreement with this figure were values of 142 ± 10 μg/g (ref. 4) and 168 μg/g (ref. 5) obtained by different methods of analysis. Examination of sieved material showed that carbon was more abundant in fine than in coarse particles. In a sample of 10084 lunar fines, particles > 60 to 140 mesh contained 92 μg/g total carbon; from 140 to 300 mesh, 183 μg/g; and finer than 300 mesh, 261 μg/g (ref. 3). This trend is consistent with that reported by Moore et al. (ref. 4).

Of the 157 ± 14 μg/g total carbon, Johnson and Davis (Section 2) have estimated that 40 ± 8 μg/g could be attributed to organic compounds. Results from extraction (Part II) indicate that virtually no organic compounds were extractable from the lunar sample by water or organic solvents. Extraction with HCl, however, yielded organo siloxanes (Section 17), which might account for some of the organic carbon.

Volatile Carbon Compounds

Acid treatment. In experiments designed to detect metallic carbides, gases derived from lunar samples by acid hydrolysis were initially examined with a low-resolution MS. Ions in the spectra that were not at least an order-of-magnitude higher in abundance than those in spectra of instrument background and control blanks were ignored. Ions of particular significance appeared with m^+/e 15, 16, 25, 26, 27, 29, 30, 41, 42, and 43. These are ions expected to be prominent in a spectrum of a mixture of C_1, C_2, and C_3 hydrocarbons. Similar results were obtained with meteorite samples.

GC confirmed the presence of hydrocarbons. Typical chromatograms are depicted in figure 3. The excellent agreement in elution times between peaks in the samples and those in the standard gas mixture, coupled with the nonexistence of substances having similar chromatographic properties and flame-ionization detector responses, leaves no doubt regarding the identity of the C_1, C_2, and C_3 hydrocarbons.

The amounts of carbon represented in the samples by the hydrocarbons are summarized in table 4. Because of their finite vapor pressure at −195° C and their solubility in the reagent solutions, all evolved gases were never completely recovered. Therefore, the data in table 4 represent minimum values. Methane, ethene, acetylene, ethane, propene, propane, and small amounts of unidentified C_3 and C_4 hydrocarbons were obtained from the lunar fines, representing up to 21 μg/g carbon in one case and 4.9 μg/g in another. (All values in this report are calculated in μg/g as carbon.) As expected, considerably more hydrocarbons were produced from the sample of cohenite. On the other hand, yields from Mighei meteorite were lower, and methane and ethene were conspicuously absent.

When H_2S in evolved gases was removed with KOH (experiment 1, table 4), the total hydrocarbon yield was about four times greater than when $ZnSO_4$ was used (experiment 2, table 4). This difference could have been a result of sample heterogeneity since preferential solution of hydrocarbons in aqueous zinc sulfate does not seem likely.

The residue from HCl treatment of the lunar fines was extracted with boiling benzene. GC of the concentrated extract on a general purpose SE-30 column revealed no compounds in concentration greater than 10^{-3} μg/g. Although C_5 to C_{10} hydrocarbons may have been lost during concentration, higher hydrocarbons apparently were not generated during acid treatment.

Chromatograms of hydrocarbons released during mild phosphoric acid treatment of other lunar samples are shown in figure 4. The products were essentially the same, in the C_1 to C_3 region, as those derived from acid treatment of the cohenite sample and, except for the absence of acetylene, from the 10086,3 lunar fines. The amounts of carbon represented by the hydrocarbons are shown in table 5. Values for total carbon concentration determined by Kaplan and Smith (ref. 2) are included. In no instance did hydrocarbon yields attain the values found in the samples of 10086,3 fines (table 4). Probably, the conditions of phosphoric acid hydrolysis were not as favorable as those with HCl. Interestingly, total hydrocarbon yields paralleled total carbon concentrations.

Possibly, the hydrocarbons were not derived from carbides, but rather were freed from mineral enclosures by HCl treatment. Data obtained from experiments described later have some bearing on this question. During pyrolysis experiments, most of the total carbon was detected as oxides. Hydrocarbons should be as easily released from mineral enclosures as oxides of carbon;

therefore, a major portion of the hydrocarbons should have been released by pyrolysis. In fact, less than 0.6 μg/g of C_1 to C_3 hydrocarbons was produced (see below) as compared to the much higher values (table 4) produced by HCl treatment. Evidently, if hydrocarbons were trapped in mineral enclosures and subsequently freed by HCl, they could have contributed only a small fraction of the hydrocarbons in the hydrolysis products.

Heating lunar materials of different types in aqueous acids consistently yielded low molecular weight hydrocarbons. Carbides (ref. 6) appear to be the only substances that would yield hydrocarbons under such conditions. Therefore, our results, combined with mineralogic observations made by Anderson et al. (ref. 7), constitute convincing evidence for the existence of carbide carbon in lunar samples.

When gases evolved during hydrofluoric acid digestion of the lunar sample were examined by high-resolution MS, no evidence was found for hydrocarbons, carbon dioxide, carbon monoxide, or other low molecular weight products besides hydrogen sulfide. The detection limit was 8 μg/g of a single compound. GC, however, revealed the presence of a hydrocarbon mixture, similar in composition to that obtained by HCl hydrolysis (table 4), in an amount totaling 7.0 μg/g.

The absence of carbon dioxide is consistent with the observation noted in Section 19 that HCl treatment produced only trace (<5 μg/g) carbon dioxide. These results indicate that the lunar sample contained, at most, 5 μg/g carbon in the form of carbonates. Furthermore, acid treatment did not appear to free carbon dioxide or carbon monoxide from mineral enclosures. Abell et al. (ref. 8) also did not report finding carbon monoxide during hydrofluoric acid treatment. However, Burlingame et al. (ref. 5) reported 66 μg/g. Although as much as 8 μg/g could have been undetected in our experiments, it is possible that the disparate results reflect inhomogeneity in the 10086,3 Bulk A fines.

Pyrolysis

In one experiment, products from stepwise heating of lunar fines at 150°–250° C, 250°–500° C, and 500°–750° C were examined by high-resolution MS. Carbon monoxide was identified only in the 500°–750° C range and amounted to 121 μg/g of the total carbon. Up to 8 μg/g could have been produced in each of the other temperature ranges without being detected. Although no carbon dioxide was found at any pyrolysis stage by this method, a total of 24 μg/g (3 X 8 μg/g) could have gone undetected. In a second pyrolysis experiment where products were studied by GC, about 50 μg/g carbon as carbon dioxide were detected. However, since large corrections were involved in this determination, as outlined earlier, this result was primarily of qualitative value. Carbon monoxide could not be determined under the GC conditions used. The carbon dioxide determinations can be understood when the detection limits in the first experiment and the qualitative nature of the second are considered.

Apparently, carbon monoxide was the major oxide of carbon evolved during pyrolysis. Release of carbon dioxide below 500° C has been reported by Lipsky et al. (ref. 9) and Oro et al. (ref. 10). The latter group found more carbon dioxide than carbon monoxide between 300° and 500° C, but from 600° to 750° C, the carbon monoxide exceeded carbon dioxide by a factor of 10. Epstein et al. (ref. 11) reported a similar trend. In the range of 150° to 1150° C, Burlingame et al. (ref. 5) detected carbon monoxide totaling 119 μg/g and virtually no carbon dioxide. Conversely, Friedman et al. (ref. 12) reported carbon dioxide between 300° and 950° C, but no carbon monoxide. Apparently, carbon monoxide and carbon dioxide determinations were reproducible

among some laboratories but not others. Heterogeneity in lunar samples plus different laboratory procedures may have been important factors in the varying results.

Burlingame et al. (ref. 5) have suggested that the major part of the carbon monoxide detected was formed on the moon by oxidation of reduced carbon with metal oxides under the influence of meteorite impact or other energy sources and entrapped in mineral enclosures. It is also conceivable that some of the carbon monoxide generated in experiments at 1100° C or higher resulted from reduction of silicates or metal oxides by elemental carbon during pyrolysis of the sample. Some possibilities are shown below.

Reaction	ΔF° *(kcal) 1100° C*	P_{CO} *(atm)*
$SiO_2 + 3C \rightarrow SiC + 2CO$	28.5	5.4×10^{-3}
$TiO_2 + C \rightarrow TiO + CO$	12.0	1.26×10^{-2}
$FeO + C \rightarrow Fe + CO$	−11.8	74

The thermodynamic calculations indicate that the reactions could occur to a significant extent around 1100° C. (All thermodynamic data taken from ref. 13.) Confirmation of this point was provided in an experiment in which 100 mg each of lunar fines and graphite were intimately mixed and pyrolyzed at 1100° C for 1 hr, during which the mixture fused. When the carbon monoxide was combusted in oxygen, 6.0 cc (25° C, 1 atm) carbon dioxide was obtained, an amount 200 times that expected from pyrolysis of all the carbon in the lunar sample. Pyrolysis of 100 mg of graphite alone followed by combustion yielded less than 0.2 cc carbon dioxide. It can be calculated that 3.1 mg graphite was converted to carbon monoxide by 100 mg lunar material. Clearly, such a process should be seriously considered as a source of carbon monoxide both in pyrolysis experiments and on the moon. On the other hand, high-temperature conversion of carbon to carbon monoxide by way of the water-gas reaction ($C + H_2O \rightarrow CO + H_2$) at 750° C, although thermodynamically favorable ($\Delta F = -2.13$ kcal), seems unlikely since most of the water in lunar material is expected to be driven off below 650° C (ref. 11). This reaction, however, may have been significant in the genesis of carbon monoxide on the lunar surface.

In the low-resolution mass spectra of the products at each pyrolysis stage, hydrocarbon ions were not detected in abundances above instrument background. GC failed to reveal any hydrocarbons at 150°–250° C. However, between 250° and 500° C, methane and an unknown C_4 hydrocarbon appeared in concentrations of 0.03 and 0.58 μg/g, respectively. At 500°–750° C, 0.05 μg/g methane, 0.27 μg/g ethene, 0.23 μg/g propene, and 0.44 μg/g unidentified C_4 hydrocarbon were produced. Thus, from 150°–750° C, less than 0.6 μg/g carbon identified as C_1 to C_3 was generated, most of it appearing at the upper end of the temperature range. The chromatograms are reproduced in figure 5. These results are quite similar to those reported by others. Pyrolysis of lunar samples up to 400° C by Murphy et al. (ref. 14) and above 400° C by Oro et al. (ref. 10) afforded traces of methane. At 900° C, Abell et al. (ref. 8) obtained 1 μg/g methane. At 500° to 1150° C, Burlingame et al. (ref. 5) detected traces of hydrocarbons. At 510° C, Nagy et al. (ref. 15) also report traces; but at 700° C, larger unstated amounts (predominantly methane) were found. In all instances except the last, only trace amounts (≤ 1 μg/g) of hydrocarbons were produced by pyrolysis. Notably, comparison of the yields of hydrocarbons and oxides of carbon produced by pyrolysis show that gaseous carbon from lunar material was primarily in oxidized states.

Two obvious processes for pyrolytic production of hydrocarbons are thermal cracking of more complex organic compounds and release from mineral enclosures in the inorganic matrix. Trapped gaseous hydrocarbons have been freed from meteorites by Studier et al. (ref. 16) and Belsky and Kaplan (ref. 17). Another possibility was suggested by Studier et al. (ref. 18) who demonstrated that, in the presence of iron meteorite powder, hydrocarbons could be synthesized from carbon monoxide and hydrogen at temperatures above 150° C. Lunar samples contain small amounts of native iron (ref. 1), and carbon monoxide and hydrogen (ref. 11) were produced by pyrolysis up to 750° C. Therefore, all the ingredients were available for the Fischer-Tropsch-type synthesis. When a previously pyrolyzed lunar sample was reheated to 750° C in the presence of carbon monoxide and hydrogen, only traces of methane, ethene, and propene, which were absent in a control experiment, were detected (< 0.05 μg/g) by GC. Apparently, a Fischer-Tropsch reaction was not favorable. Although the reaction could account for a small fraction of the hydrocarbons generated during pyrolysis, most were probably produced by cracking organic compounds or by liberating them from the inorganic matrix.

Residual Carbon

In the experiment in which GC indicated generation of carbon dioxide during pyrolysis of lunar fines to 750° C, the residue contained 63 μg/g carbon. When a pyrolysis residue from a similar experiment was heated to 1050° C and the resulting gases combusted to carbon dioxide, 100% of the initial total carbon was accounted for. Direct combustion of the residual material produced no additional carbon dioxide. Apparently, no carbon remained after pyrolysis at 1050° C. In light of the experiment involving heating of lunar fines and graphite described previously, the results of pyrolysis and combustion at 1050° C suggest some residual carbon in the form of elemental carbon. Burlingame et al. (ref. 5) reported that, after digesting a sample of lunar fines in hydrofluoric acid, pyrolysis of the residue to 1100° C yielded 119 μg/g carbon in the form of carbon monoxide. Although, as they suggest, the carbon monoxide could have been freed from the residual silica matrix by pyrolysis, it seems equally possible that some was produced by reduction of silica by elemental carbon.

Material remaining after repeated treatment of the lunar sample with hydrochloric and hydrofluoric acids contained 36 ± 6 μg/g carbon in duplicate experiments. Since carbides would have been removed by this treatment, the residual carbon should be largely composed of elemental carbon (graphite). The presence of carbides in the pyrolysis, but not hydrolysis, residues would account for part of the 27-μg/g difference in residual carbon content.

SUMMARY AND CONCLUSIONS

Pyrolysis and hydrolysis experiments indicated that the carbon in the 10086,3 Bulk A lunar fines is present in the form of carbide, carbon monoxide, and carbon dioxide (or substances that yield oxides of carbon during pyrolysis or hydrolysis), and possibly elemental carbon. A crude estimate of the carbon distribution in a sample of fines is as follows: Carbon dioxide accounted for about 50 μg/g carbon in a pyrolysis experiment. The pyrolysis residue contained 63 μg/g carbon, of which some was probably elemental carbon and as much as 21 μg/g was carbide. A sum of 153 μg/g is obtained. By comparison, the direct measurement of total carbon yielded 157 ± 14 μg/g. Although carbon monoxide was not determined in this instance, another pyrolysis experiment (in which it was identified by MS) showed that it should have been present. Control

experiments indicate that the carbon compounds obtained from the lunar sample were indigenous to the lunar surface and not introduced as laboratory contamination.

The cosmological significance of lunar carbon is not completely understood at present. Since high temperatures may have been involved in the formation of materials in the Sea of Tranquility (ref. 1), products of primordial organic synthesis are not likely to have survived. This is consistent with the low concentration of organic compounds found in the samples.

Exposure of carbides, carbon monoxide, carbon dioxide, elemental carbon, hydrogen, and metals and metal oxides to sufficiently intense thermal and/or radiation energy on the moon's surface could convert some of these substances to organic molecules. Entrapment in the inorganic matrix could possibly preserve some of the products from further loss by volatilization or radiation-induced destruction.

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We thank Mr. Fritz Woeller and Mr. Edward Ruth for their valuable assistance in part of this work.

4. CARBON AND SULFUR ISOTOPES *Ian Kaplan and John W. Smith*

CARBON ISOTOPIC COMPOSITION

The $\delta^{13}C$ composition of the total carbon of this sample was determined to be +20/mil relative to the Peedee Belemnite (PDB) standard. This $\delta^{13}C$ value is anomalously heavy compared to total meteoritic carbon with a range of −4 to −25/mil, and terrestrial carbon with a range of +2 to −30/mil. The carbon of this lunar sample is not as enriched in ^{13}C as the carbonate phase of meteorites, which range from +40 to +70/mil. For a complete discussion of this and other isotopic determinations on lunar samples, see Kaplan and Smith (ref. 2).

SULFUR ISOTOPES

Gases evolved during the hydrolysis steps of the general scheme of analysis (fig. 1) contained high concentrations of sulfides with unusually heavy isotopic compositions. This finding prompted additional experiments. Total sulfur was determined on a separate 3-g sample of lunar fines by oxidation of sulfides to sulfates with bromine and aqua regia. After the metal (iron) hydroxide was precipitated with ammonia, the solution was filtered, reacidified, and brought to boiling. Barium chloride solution was added, and the precipitated barium sulfate was removed by filtration after standing overnight. The barium sulfate was converted quantitatively to barium sulfide by reduction with graphite powder at 1050° C for 1 hr in a quartz crucible under nitrogen. Once cooled, the barium sulfide was dispersed in deoxygenated water and rapidly filtered into 5% silver nitrate solution for conversion to silver sulfide, which was oxidized to sulfur dioxide for MS analysis.

Sulfur in samples from the Canyon Diablo, Murray, and Pueblito de Allende meteorites was analyzed by reacting these samples under vacuum with either 85% phosphoric acid or 2N HCl (ref. 2). The sulfide gas generated was precipitated as silver sulfide, also converted to sulfur dioxide for MS analysis.

The concentration and isotopic composition of sulfur in the lunar fines and in three meteorites are given in table 6. There was little variation in the sulfur content of the lunar fines,

whether determined by acid hydrolysis or oxidation: contents of 640, 670, and 690 μg/g were found by three separate experiments.

Values for $\delta^{34}S$ show very high enrichment of the heavy isotope in the fines compared to meteoritic sulfur. In general, values for meteoritic troilite produced by HCl treatment fall within ±1/mil of a Canyon Diablo standard. The data here show reasonably consistent results for the lunar material analyzed by acid treatment and by aqua regia oxidation, but a somewhat lower $\delta^{34}S$ for the sample treated by phosphoric acid. To determine if this difference was due to some experimental artifact, samples from two intact meteorites (Murray and Pueblito de Allende) and troilite from Canyon Diablo meteorite were reacted with HCl or H_3PO_4. The results in table 6 show that variation can occur, both in amounts of sulfide released and in isotope ratio. This finding is interpreted as partly due to inhomogeneity and partly to multiple forms of metal sulfides being differentially soluble in the two acids. In this set of experiments, the greatest variation for $\delta^{34}S$ is +1.1/mil relative to the standard. Therefore, the values falling around +8/mil are considered real and the value of 5.4/mil obtained by H_3PO_4 treatment represents heterogeneity, e.g., possible inclusion of some larger grain fragments. Examination of more samples of lunar fines is necessary before an explanation of these observations can be offered. Certainly, the fines are heavily enriched in ^{34}S. The degree of enrichment apparently is not constant.

5. MICROFOSSILS *J. William Schopf*

Lunar rocks, chips, dust, petrographic thin sections, acid-resistant residues of lunar dust, and portions of the Apollo 11 bioquarantine samples were examined in an effort to detect morphologic evidence of living systems. Biogenic materials (e.g., cellulose fibers), representing terrestrial contamination, were observed during these studies; no evidence of lunar organisms, either extant or extinct, was detected.

This section (1) summarizes the observational techniques used in these studies, (2) documents the occurrence of particulate organic contamination in portions of the Apollo 11 samples, (3) catalogs the morphological diversity exhibited by shaped glassy particles present in the lunar dust, (4) outlines a possible history for such shaped glasses, and (5) records the occurrence of microscopic pseudofossils observed in petrographic thin sections. This account is more descriptive than interpretive, and cursory rather than exhaustive: Its chief intent is to note the occurrence of several interesting morphologic features of the Apollo 11 samples as a useful basis for subsequent detailed studies.

MATERIALS AND METHODS

Studies were made with a light microscope (L) at magnifications ranging from 4X to 1500X and, after coating specimens with a thin gold-palladium film, with a scanning electron microscope (SEM) at magnifications ranging from 30X to 30,000X. The following samples were examined: (1) lunar dust (sample 10086,18 from the bulk sample box), divided into four size-fractions by sieving ($> 246\ \mu$, 246–124 μ, 124–74 μ, $< 74\ \mu$), L and SEM; (2) residue resulting from dissolution of lunar dust in hydrofluoric and hydrochloric acids, L; (3) surface of rock chips from the exterior and interior of a microbreccia (sample 10002,54 from the bulk sample box), and fragments of these chips, L and SEM; (4) petrographic thin sections of microbreccias (samples 10019,15, 10046,56, 10059,32, 10059,37, 10061,27, 10061,28, and 10065,25), L; (5) sample

10086, Bulk A fines, L; (6) rocks, chips, dust, and bioquarantine samples (including portions of both cores), L (ref. 1).

PARTICULATE ORGANIC CONTAMINATION

Preliminary studies of the Apollo 11 samples at the Lunar Receiving Laboratory, prior to the termination of quarantine and the release of samples to principal investigators, revealed the occurrence of particulate organic contamination in several portions of the lunar sample. Fine-grained dust from the bulk sample box, observed at the science observer port in the F-201 chamber in the Vacuum Laboratory, contained teflon fragments and several organic fibers, 10 to 30 μ in diameter. Dry-mounted preparations of lunar dust from the documented sample box, observed in the Bio-preparation Laboratory, contained numerous shreddy organic fibers, 1 to 8 μ in diameter (NASA photographs S-69-45783, -45863, -45869); similar birefringent filaments, as large as 20 μ in diameter, were detected in dry-mounted preparations of core samples used for bioquarantine tests (NASA photographs S-69-45804, -45844, -45872).

Lunar dust studied at UCLA, packaged at the Lunar Receiving Laboratory under conditions apparently identical to those used in the preparation of samples for distribution to principal investigators performing organic chemical analyses, contained similar organic fibers (plates 29, 30), although their concentration seemed much diminished as compared with that initially observed during studies by the Lunar Sample Preliminary Examination Team (LSPET, ref. 1). Birefringent organic filaments were also present in the mounting medium (but *not* within mineral grains) of several of the petrographic thin sections examined.

The rather pervasive presence of this particulate organic contamination, primarily fibers derived from Kleenex, lens tissue, and similar paper products, should be considered in evaluating results obtained by analytical techniques designed to detect carbon and carbon compounds in the Apollo 11 samples.

MORPHOLOGY OF SHAPED GLASSY PARTICLES

Glassy particles constitute the predominant component of the lunar dust (ref. 1). Approximately 50 to 70% of the dust considered in the present study is of glassy composition, mostly botryoidal, subangular, or angular fragments (plates 31, 32); about 1/4 to 1/5, chiefly concentrated in size-fractions with diameters less than 0.5 mm, exhibits spherical (plates 11, 13, 15); spheroidal (plates 9, 10), ellipsoidal (plates 2, 3), discoidal (plates 6, 12) or lenticular (tear-, dumbell-, or rod-shaped) form (plate 1). The variety of colors displayed by these shaped glassy particles (clear, grayish-white, yellow, amber, orange, brownish-red, and rather less commonly, green or blue), and their variable indices of refraction (ref. 1), reflect a rather wide range of composition.

Spheroidal glasses, the dominant form of shaped particles present in the dust, vary in diameter from several millimeters to less than 1 μ; commonly, their surfaces are shiny or specular. Short, stubby, granular appendages (plate 4) are present on many of these particles; uncommonly, two (plate 9) or more such appendages are present on the same spheroid. These appendages are coherent, and are firmly fixed to the spheroids; they are composed of fine granular material similar to that irregularly distributed on most glassy surfaces (plates 1, 4, 9, 32). A few spheroids exhibit very irregular surfaces (plate 5) composed of multiple layers of glasses and particulate debris.

Several of the spheroids are partially broken, revealing interior voids surrounded by a thick shell (plate 7) or solid interiors displaying conchoidal fracture patterns (plates 8, 17, 18).

The surface texture of the shaped glasses varies gradationally from essentially smooth, with large irregular vugs (plates 1, 11, 19); to vesicular, with an outer shell partially obscuring a labyrinth of interconnected chambers (plates 20, 28); to rather regularly dimpled, with pits of fairly constant size (plates 15, 16, 21–23); to both dimpled and papillose, with numerous pits and small hemispherical papillae (plate 24); to predominantly papillose, covered with glass droplets of varying diameters (plates 13, 14, 25–27) occurring in chains (plate 26) or with larger papillae surrounded by rings of smaller droplets (plate 25). Many spheroids exhibit relatively large surficial craterlets (plates 10, 15) containing radially oriented fracture patterns.

Glass spheroids and ellipsoids, apparently identical to those occurring in the lunar dust, are also present in microbreccias. Unlike glass droplets of terrestrial volcanic origin, these particles (plates 39–41) are markedly inhomogeneous in both texture and composition; the occurrence of spheroidal cavities, of included minerals and glasses of varying colors, refractive indices and degrees of devitrification, and the common presence of wispy, ribbonlike flow structures, are indicative of a complex history of development.

ORIGIN AND DEVELOPMENT OF SHAPED GLASSES

Based on the data presented above, the following sequence of events is suggested for the genesis and development of the shaped glassy particles:

1. Clouds of molten glasses and particulate debris produced by meteoritic impact, and possibly in part by volcanism (ref. 19) were ejected from the lunar surface.
2. The sphericity of these particles indicates that they were produced in free flight, primarily molded by forces of surface tension; the occurrence of dumbell-shaped particles (plate 1) and the presence of equatorial flanges on many spheroids (plates 2, 6, 10–12) indicate that rotational components were important in their formation.
3. Degassing occurred as the particles solidified, producing internal voids and vesicular, pitted surface textures; surficial glass papillae were probably also formed by this process (since some appear to represent "frozen" bubbles), but the majority are the result of collisions with smaller glassy droplets that adhered to the larger spheroids. Fusion of several spheroids, of differing compositions and degrees of solidification, followed by rapid quenching, led to the formation of complex glassy aggregates (e.g., plates 39–41).
4. Some solidified spheroids were impacted at high velocity by particles within the ejected cloud, producing small, well-defined craterlets; other spheroids were chipped, fractured, and abraded by such collisions (plates 7, 8, 17).
5. Upon impacting the lunar surface (and also within the ejected cloud), fine angular particles became embedded in partially molten glass surfaces; particulate appendages (plates 4, 9) were apparently sintered to spheroids by such impacts, and the irregular surficial layers of some spheroids (plate 5) probably reflect tumbling and rolling in lunar dust.
6. Subsequent shock welding and fusion of dust by meteoritic impacts resulted in the inclusion of these shaped glass particles in microbreccias.

MINERALOGIC PSEUDOFOSSILS

Partially devitrified areas within lunar glasses contain complex microcrystalline structures that vary in form from highly angular, obviously crystalline and unmistakably mineralogic (plates 37, 38), to globular, actinomorphic, possibly interconnected (plate 36) structures of variable symmetry (plates 33–36) that are superficially similar in morphology to some terrestrial microorganisms. Minute crystalline inclusions (plates 41, 44), glassy beads (plate 42), and flow structures in glassy phases (plates 39–41) also mimic some biogenic structures. Most such forms are comparable to the "globularities," "microlites," and "trichites" (ref. 20) typical of terrestrial glassy igneous rocks (refs. 21 and 22); the possibility of misinterpreting such crystalline phenomena as representing microfossils has been pointed out by Bramlette (ref. 23) and by Cloud et al. (ref. 24). Finally, in addition to containing the fibrous contaminants noted above, the mounting medium of several of the petrographic thin sections studied contains spheroidal vugs that were initially filled with the fine-grained abrasive used in thin section preparation; in some cases (plate 43), the abrasive has been extruded from such bubbles, producing interesting (and entirely nonbiologic) artifacts.

SUMMARY

The salient results of these studies may be summarized as follows:

1. Micropaleontological investigations of a variety of lunar samples (including rocks, chips, dust, petrographic thin sections, acid-resistant residues, and bioquarantine samples) using L and SEM have yielded no evidence of extant or extinct lunar organisms.
2. Preparations of lunar dust from the bulk sample box and from the documented sample box contained particulate organic contamination (e.g., cellulose fibers) apparently introduced during sample processing at the Lunar Receiving Laboratory; some samples distributed to principal investigators contained similar contaminants. This potential source of organic matter should be considered in evaluating reports of carbon and carbon compounds in the Apollo 11 samples.
3. As an ancillary product of this search for biogenic structures in lunar materials, data bearing on the origin and development of shaped glassy particles in lunar dust and microbreccias have been obtained; in addition, these studies have documented the occurrence of several types of microscopic pseudofossils in the Apollo 11 samples.

ACKNOWLEDGMENTS

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6. INORGANIC STRUCTURES

Delbert Philpott, Charles Turnbill, and Elso Barghoorn

The extremely low carbon content of the rocks and fine-particle remnants (dust) of the lunar regolith from the Sea of Tranquility indicated little or no possibility that the moon had ever evolved a biosphere during the course of its history. This a priori conclusion has been confirmed by careful examination of rock chips (microbreccia), thin sections (microbreccia), and dust, as outlined in Section 5. Morphological and optical properties of discrete objects in the lunar material, at all

levels of observation employed in this study, show total absence of structure that can be interpreted as biological in origin. The lunar fines examined in this work were virtually devoid of terrestrial contaminants.

Although no morphological evidence of biological systems was detected, numerous interesting inorganic structural entities were found in the investigation of lunar sample material. A 2-g fraction of lunar fines and a 0.7-g sample of breccia have been photographed using L and high-resolution electron microscopy. Surface features were studies using SEM. Further investigative procedures included preparation of petrographic thin sections from the lunar sample and some identification with electron diffraction and X-ray probe analysis.

Initial observations on the loose sediment showed sharp angular fragments (plate 45) glassy spheres (plate 46), and globular bodies (plate 47). These lunar spheres ranged in size from 0.05 μ to 1 mm. Their distribution was quite heterogeneous, which seems to be a characteristic of the entire sample. Since fractured glass was also present, maximum sphere size was difficult to determine. The melted portion varied from spherical to cylindrical and included portions in which fines were embedded in the spheres. Heterogeneous sphere interiors were common, varying from hollow to crystalline as evidenced by their effect on polarized light. No liquid inclusions were seen in any of the spheres. The spheres generally had a few pores (plate 48) on their surfaces, and the size of the pores, or holes, appeared to increase with increasing sphere size. The spheres often have a shell-like surface resembling an onion with several layers partially removed. Observation of individual particles was facilitated by mild sonication, which separated the particles for better observation. The rest of the fine material consist of irregular shapes with sharp edges resembling fractured faces. The crystallinity of these particles is easily established by observation in polarized light and by using electron diffraction.

Glassy spheres were produced from the jagged fines by concentrating the electron beam in the vacuum of the electron microscope on the individual particles. Each particle was observed by electron diffraction during heating. The diffraction pattern disappeared instantly as the particle melted, and no further change occurred. The lunar spheres also lack an electron diffraction pattern. The theory of melting and cooling in free flight is compatible with the present observations. Quick zoning, crystalline inclusions, and holes from possible degassing would all be expected from fast cooling. The presence of spheres with fines embedded on one face (plate 49) suggests that these spheres impacted before their interiors cooled. For example, melted ejecta from meteoric impact would send material for different distances, and some of it could be expected to impact before complete cooling. Micrometeorites could produce holes, too.

No weathering is evident in the fines or breccia; only fracturing is present. This is not surprising due to the lack of water or wind and is consistent with other observations.

Many of the particles were electrostatically charged. This facilitated hand separation of different phases since all but the larger particles would jump to a metal or wooden probe. The charge was often strong enough to prove disadvantageous for metal shadowing, since the charge could deflect the oncoming metal, and particles free of metal could be observed after the shadowing process.

7. MINERALOGY *Klaus Keil, F. D. Busche, and Konrad Krauskopf*

A cursory examination of the bulk lunar sample by light microscopic techniques showed the presence of dominantly plagioclase feldspar and pyroxene with minor amounts of olivine and ilmenite. Glass spherules of unknown composition were also observed.

An aliquot weighing about 0.5 g of lunar fines was examined in detail. The sample was sieved through a set of nylon sieves and the +100-mesh fraction was studied under the stereomicroscope. Six fractions consisting largely of feldspar (and anorthositic rock fragments), pyroxene, olivine, rock fragments, glass spherules, and glass fragments were hand picked for preparation of polished thin sections. These sections were studied in detail with the optical microscope and the electron microprobe X-ray analyzer. These studies reveal that the sample consists of fragments ranging from fine-grained to coarse-grained basaltic-type rocks to anorthositic rocks containing largely anorthite and augite. The sample also contains the minerals plagioclase, ranging in composition from labradorite to anorthite, and pyroxene, ranging in composition from augite to subcalcic augite to pigeonite and pyroxmangite. Olivine occurs in accessory amounts. Ilmenite is the dominant opaque phase, but minor amounts of metallic nickel-iron of meteoritic origin and troilite were also observed.

The presence of metallic nickel-iron of typical meteoritic composition suggests that at least part of the loose surface material is of impact origin. However, the amount of meteoritic material present in the sample is small (probably <1% by weight); hence, it is concluded that contributions from common meteorites have not appreciably altered the bulk composition of the loose surface fines. Glass spherules and irregularly shaped glass fragments are common. Composition of the glass spherules varies considerably and is probably in large part due to differences in composition of the parent rocks and to different mixing ratios of the dominant minerals plagioclase, pyroxene, and ilmenite. Quantitative electron microprobe analyses of various phases from the loose fines 10086,3 are listed in tables 7 through 12. The minerals observed in the sample do not appear to be altered by chemical weathering. Furthermore, no evidence of significant amounts of hydrous minerals was found in any of the sections studied. The textures and compositions of the rock fragments studied are typical of comparatively rapidly cooled rocks and are analogous to terrestrial volcanic or hypabyssal rocks.

Part II

EXTRACTION AND HYDROLYSIS

8. PREPARATION OF SAMPLES FOR ANALYSIS

Keith A. Kvenvolden and John W. Smith

The major portion of the fine-grained lunar sample material was extracted with lipid and aqueous solvents and was hydrolyzed with hydrochloric acid according to the scheme shown in figure 1. The analytical procedures used were based on the assumption that minimum handling of both solids and liquids was necessary for satisfactory completion of the analysis. In this sequential scheme, which involved a minimum of glassware, the solid lunar sample was retained in all steps in the vessel in which it was originally placed (fig. 6). Solutions were recovered from the solid by centrifugation and decantation. Addition of extracting solvents to the sample was calculated by weight so that no volumetric measuring glassware was needed. A blank composed of quartz sand fired at 1000° C for 48 hr was analyzed in parallel with the lunar sample to provide a basis for determining the extent of any laboratory contamination that might have occurred accidently.

In preparation for extraction, all glassware was carefully washed in Alconox detergent and hot water, rinsed, and placed in a bath of sulfuric acid and sodium dichromate at 90° to 100° C for at least 1 hr. Each piece of glassware was rinsed with single-distilled water and finally with triple-distilled water and dried in an oven at 150° C. The glassware was stored in covered stainless steel trays. Before use, each piece of glassware was rinsed with the solvent that was to follow in the analysis. All solvents were distilled and were carefully evaluated prior to use. Evaluation of solvents involves taking the solvents through the analytical scheme and determining the level of background contamination that could be expected during an actual analysis of the lunar sample.

BENZENE-METHANOL EXTRACTION

In a stainless steel glove box over a glass tray, 54.6 g of very fine-grained, black lunar sample was transferred, by means of a stainless steel spatula, from a weighing bottle to a 500-ml centrifuge bottle, modified with an ₹ 34/28 ground glass joint with teflon sleeve. To the sample were added 82 g of distilled benzene-methanol (9:1).[1] This mixture was sonicated for 15 min with stirring in an ultrasonic tank.[2] The mixture was centrifuged[3] at 2000 rpm for 10 min. To remove suspended

[1] Pesticide quality, benzene (BX 219) and methanol (MX 484) supplied by Matheson, Coleman & Bell; distilled in a Kontes K-502500, 1.25 X 50-cm, vacuum-jacketed column packed with 6-mm glass helices, still head K-518500, and takeoff rate of about 1 ml/min.

[2] American Process Equipment Corp. special model ultrasonic tank, 22-kHz frequency, powered by APEC Acoustica at 30% full power.

[3] International R-6 operated at 20°.

particulate matter, the extract was filtered through a 9- X 80-mm plug of precleaned and extracted glass wool in a glass tower. The solid sample was washed with benzene-methanol, centrifuged, decanted, and filtered two additional times. The final weight of extract solution recovered was 196 g. Of this final weight, 151 g were used for hydrocarbon analysis and 45 g were used for porphyrin analysis. This final extract had a very slight golden cast due perhaps to very fine suspended material that passed the filter.

A sand blank weighing 59.0 g was processed in exactly the manner as the sample. The sand was Standard Ottawa (washed and ignited for boats), Matheson, Coleman & Bell SX 75, refired at 1000° C for 48 hr and cooled in a dessicator over Drierite. Final weight of extract solution recovered was 197 g, of which 159 g were used for hydrocarbon analysis and 38 g for porphyrin analysis.

Residual solvent (about 17 g) remaining with the solid was removed by rotary evaporation against an aspirator vacuum. The sample dried to a fine black powder; the sand blank also was dried. The Calab Model C rotary evaporator used for this process was connected to the water aspirator through two 500-ml special Calab cold finger condensers cooled with liquid nitrogen. The glassware train for evaporation consisted of the 500-ml centrifuge bottle with ⅋ 34/28 inner joint; a filter consisting of a No. 25 teflon O-ring joint with ⅋ 24/40 connectors and modified to hold a coarse glass frit and a 5-μ Millipore teflon filter; and a ⅋ 24/40 splash head (fig. 6).

H_2O EXTRACTION

The dried sample and 90 g triple-distilled H_2O were sonicated with stirring for 15 min, centrifuged as before, and decanted through glass-wool filters. The water was Alhambra water (distilled water from a local vendor), redistilled in a Kontes W-2 all-glass still. The sample was washed, centrifuged, decanted, and filtered two more times. The final weight of extract recovered was 219 g, which was of grayish color due to very fine particulate material that had passed the glass-wool filter. About 18 g water remained with the solid sample.

The sand blank was treated in a similar manner. About 230 g H_2O were added to the sand and about 214 g were recovered.

1N HCl EXTRACTION

To the H_2O wet sample were added 136 g of 1N HCl. The HCl solutions were prepared by bubbling HCl gas (Matheson) through triple-distilled water and diluting to proper normality. This mixture was placed in an aluminum heating block at about 125° C, and the sample was refluxed for 1 hr. The vent of the relux condenser was connected to a train of traps. Dry, deoxygenated nitrogen was passed through the entire system during the refluxing. Nitrogen was passed through an oxygen-removing, gas-purifying furnace (Sargent S 36517 and S 36518) and through a drying tower containing Drierite, 5Å molecular sieve, and Ascarite. The train was designed to remove CO_2 and H_2S from the effluent gases. The train consisted of seven traps: (1) a safety trap to protect the sample from the substances in the train, (2) 250-ml gas scrubber with H_2O, (3) silver nitrate-containing gas trap, (4) phosphoric acid/P_2O_5-containing gas trap, (5) gas trap immersed in liquid nitrogen, (6) Ascarite U tube, and (7) a 500-ml gas scrubber with H_2O (fig. 7).

Immediately after the hydrolysis of the sample began, H_2S was detected. After hydrolysis the sample was cooled, centrifuged as before, and decanted through the same glass-wool filters used for the H_2O extract. The sample was washed, centrifuged, decanted, and filtered two more times.

The total weight of 1N HCl used for refluxing and washing was about 255 g. About 219 g of extract were recovered; the extract had a light bluish hue.

The sand blank was hydrolyzed under the same conditions. About 265 g of 1N HCl were used for hydrolysis and washing; approximately 264 g of the extract were recovered.

6N HCl EXTRACTION

To the sample were added about 170 g of 6N HCl. The sample was hydrolyzed at about 125° C under reflux for 19 hr. During the first 16 hr of hydrolysis, effluent gases, including H_2S, were trapped as described for the 1N HCl extraction. After hydrolysis the sample was cooled, centrifuged as before, and decanted through the same glass-wool filters used for the 1N HCl hydrolysis. The sample was washed, centrifuged, and decanted two more times. Because the filtrate appeared free of any particulate material, the washes were not filtered. The total weight of 6N HCl used was approximately 295 g, of which 207 g were recovered; this extract was bright bluish-green.

The sand blank was hydrolyzed under the same conditions. Of the 283 g of 6N HCl used in this procedure, 266 g were recovered; this hydrolysate was bright yellow.

The sample was dried by rotary evaporator used in conjunction with aspirator vacuum, 80°–90° C water bath, and a single-finger condenser in liquid nitrogen. Evaporation was to have been done with the previously described apparatus. However, proper vacuum could not be established during the actual analysis, and the system was modified as follows. The splash head and teflon disc were removed. A single-finger trap in liquid nitrogen was placed between the sample and the aspirator. Because the teflon disc was removed, a small portion of the dried sample was pulled into the finger trap; this material was recovered and saved. As the liquid was removed from the sample, the sample appeared to become more powdery. The sand blank was dried by the same system.

BF_3/MeOH EXTRACTION

To the dried sample was added 82 g of a 7% solution of BF_3 in methanol. This mixture was refluxed at 90° C for 4 hr. (A solution of 14% BF_3 in methanol was prepared by bubbling 125 g BF_3 (Matheson) into 1000 ml distilled methanol; the 7% solution was obtained for the 14% solution.) After the mixture cooled, the sample was centrifuged as before and the extract decanted through the glass-wool filters that had been used for the benzene-methanol extract. The sample was washed with methanol, centrifuged, and decanted two more times. The total weight of solvent used was 179 g, of which 153 g of a bright green solution were recovered.

The sand was treated in a similar manner. About 205 g of solvents were used, and 182 g of a colorless solution were obtained.

The sample and sand blank were dried as described for the 6N HCl solution, except that a teflon filter, which had been eliminated during the 6N HCl evaporation, was placed in the system for the evaporation of methanol. The dried sample residue was greyish and very powdery. Its total weight was 37.6 g.

Each of the extracts and hydrolysates was examined in detail, as outlined in the following sections.

9. PORPHYRINS *Gordon Hodgson, Etta Peterson, and Berthold Halpern*

This study was undertaken to determine (1) if porphyrins are present on the moon; and (2) if possible, the significance of such compounds, especially within the context of chemical evolution and the origin of life.

MATERIALS AND METHODS

The basic analytical method was to extract lunar soil with organic solvents and to search for porphyrins using optical methods, assisted to some degree by chemical and physical transformations. Spectral methods were direct spectrofluorometry and spectrophotometry, using a Turner 210 spectrofluorometer and a Cary 14 spectrophotometer.

Fluorescence detection limits were lowered to less than 0.1 ng by a recent development of an in situ method for demetallating weakly fluorescing or nonfluorescing metalloporphyrins (ref. 25). Major improvements in magnetic circular dichroism (MCD) instrumentation coupled with computer reduction of data to suppress background noise made MCD appreciably more sensitive than absorption spectrophotometry; therefore, this technique (described in Section 10) was used to try to detect lunar porphyrins. A detailed sketch of the analytical steps is shown in figure 8.

A 45-g aliquot of the 196-g benzene-methanol lunar sample extract was analyzed. To check the analytical techniques at all stages, a procedural blank derived from the extraction of an equal weight of fired sand was developed and analyzed in the same manner as the lunar sample.

The 45-g aliquot of solvent extract was first examined directly by fluorescence. As received, it showed no spectral features. By concentrating it to 1 ml on a rotary evaporator under vacuum, an intensification factor of about 40 was attained. This solution showed weak-fluorescence emission bands at 550, 600, and 630 nm. Clear-cut excitation peaks were observed at 390 and 455 nm, with the latter the more intense, as shown in figure 9. Corresponding blank data showed no peaks, only a low background.

Absorption spectrophotometry gave only a gently rising background curve with no spectral features, even when the concentrated solution and 0- to 0.1-OD-range slidewire were used. It was necessary to centrifuge the lunar solution to precipitate finely dispersed solid particles before spectral examination. The blank solution was equally featureless, with a small increase in absorbance toward the ultraviolet.

MCD gave minor spectral responses on computer averaging of multiple scanning, but these were not readily attributable to porphyrin compound.

All of the foregoing data were obtained in nondestructive approaches, and the next stage was to subject the lunar extract to more specific spectrofluorometric analyses through chemical alteration of the pigments involved. The same aliquot was put through a demetallation procedure involving methanesulfonic acid (MSA) to enhance the fluorescence of porphyrins, either by simply changing them or by demetallating them to the diacid form. To afford a measure of control on the interpretation of the results of the procedure, this portion of the sample was split into two additional aliquots: a one-fifth portion and a four-fifths portion. Each was demetallated separately.

One-Fifth Demetallation

Before addition of MSA, the fluorescence of the pigment now transferred to ether was determined and found to be substantially weaker proportionately than it was at the time of initial

examinations. This reduction was attributed either to degradation of the pigment or to quenching of its fluorescence during handling, perhaps through oxidation or metal complexing. MSA was added in small increments; after 3% MSA was reached, an excitation band at 410 nm emerged, which increased in intensity to 7% MSA. Beyond this point the band was masked by background fluorescence, as confirmed by a blank run on reagents. The increase in fluorescence is illustrated in figure 10.

After increasing the MSA content to about 72%, the products of the reaction were treated to recover any free-base porphyrin present. Neutralization of the MSA solution with sodium acetate and partitioning it with ether transferred such free-base porphyrins to the ether layer, and faint excitations at 385 and 450 nm were evident. Transfer to 6N HCl was the next step. A weak peak was observed at 390 nm and this was interpreted tentatively as a porphyrin Soret band.

To verify its identification as porphyrin, the colored substance was complexed with copper to quench its fluorescence. This was done by transfering it to glacial acetic acid and adding a copper salt (cupric sulfate). The apparent Soret band disappeared after a few minutes at room temperature.

Since the foregoing data on a small aliquot of the sample indicated the presence of porphyrins, the same reaction was carried out on the larger four-fifths aliquot.

Four-Fifths Demetallation

Addition of small volumes of MSA resulted in emergence of substantial excitation bands at 410 nm. Principal increase of fluorescence was evident for 5 and 7% concentrations, and the MSA threshold appeared to be about 2% MSA. Unknown organic matter interfered to some extent with the reaction. The reaction was terminated at 67% MSA, with no additional MSA thresholds being detected.

As before, any free-base porphyrins present were transferred to ether to remove MSA. In ether, broad excitation bands were observed at 390 and 415 nm for emission at 630 nm.

Extraction of the ether layer with 6N HCl in the cell produced an aqueous layer that exhibited fluorescence emission peaks at 600, 628, and 685 nm. A strong 385-nm Soret peak was evident, and non-Soret peaks were apparent at 517 and 550 nm. These spectra are illustrated in figure 11. Figure 12 shows confirmation of the position of the emission bands through multiple scanning at various emission wavelengths.

After exhaustive spectral examination in both HCl and ether as summarized in table 13, and after determination of ether-acid partition (4N HCl), the porphyrin pigments were complexed as before with copper; figure 13 shows the complete suppression of the fluorescence of the porphyrin.

The procedural blank was put through the same demetallation and recovery procedure and showed no indication of porphyrins. In addition, a number of special tests were made to test for contamination of the samples, involving specific glassware and reagent and handling steps. All tests were negative.

The major portion of the 151-g benzene-methanol extract of lunar sample was designated for chromatography to yield fractions for alkanes, aromatic hydrocarbons, and fatty acid esters through elution on silica gel with hexane, benzene, and methanol, respectively. The benzene eluate (see Section 13) on ultraviolet examination showed no aromatics at wavelengths above 300 nm, nor did any appear in fluorescence. Nonpolar porphyrins were sought in this benzene eluate, and there was some indication of 390- to 450-nm excitation, weakened perhaps by quenching as noted above. A demetallation analysis of this fraction showed a small amount of porphyrin, and the tentative

conclusion is that the bulk of the lunar porphyrins does not elute with benzene from silica gel under these conditions.

RESULTS AND INTERPRETATION

The salient features of the foregoing analysis appear to be:

1. Fluorescent compounds were present in direct organic-solvent extracts of the lunar soil.
2. Free-base porphyrins were recovered from the extract through reactions designed to demetallate porphyrins.
3. Abundance was estimated to be about 10^{-4} μg/g sample.
4. Unless untested contamination took place, the porphyrins are indigenous to the lunar soil.

One possible explanation for the presence of minute quantities of porphyrins in the fine lunar materials involves the generation of porphyrins on the rocket exhaust at the lunar surface. Fortunately, tests of rocket exhaust had been made prior to the Apollo 11 mission.

Samples of rocket exhaust were made available from the test firing reported by Simoneit et al. (ref. 26). These comprised samples from trap A, a liquid nitrogen-cooled trap for the exhaust gases; and trap E, a trap containing dunite. Trap A material showed an intense-fluorescence background on which a broad excitation band (in methanol and ether) appeared at 450 nm for emission in the 600- to 700-nm range. In HCl, the exhaust products turned a bright yellow, and an excitation band at 390 nm was clearly present. Absorption spectrophotometry yielded a featureless spectrum except for a rising baseline due to the scattering effect of the yellow color. MSA demetallation of the exhaust material (i.e., without any chemical fractionation) showed an excitation feature appearing at 5% MSA located at 410 nm. This spectral feature persisted until 23% MSA was reached, after which a much stronger feature emerged at 385 nm and shifted gradually to 392 nm. Attempts to recover free-base porphyrins from the foregoing aqueous acid layers were unsuccessful.

Trap E gave similar results. Extraction of the sample was carried out in the same manner as the lunar sample. A broad excitation band was evident at 450 nm on an intense background, and the addition of MSA gave typical demetallation results for metalloporphyrins. At 25% MSA, a strong peak emerged and increased in intensity with increasing acid content until 50% MSA was reached. Final location of the band was at 390 nm, and the corresponding emission peak was at 595 nm. MCD analysis of material extracted from trap E showed a large number of compounds, but none could be definitely identified as a porphyrin.

To confirm and extend the previous results and to demonstrate adequate control over laboratory procedures, another set of samples was analyzed. Approximately 10 g each of the same lunar soil, trap E dunite, Pueblito de Allende meteorite, and Ottawa sand were extracted with 9:1 solutions of benzene-methanol.

Figure 14 shows fluorescence excitation curves for the extracts. MSA demetallation is illustrated in figure 15. Figure 16 shows the results of procedures for the recovery of free-base porphyrins. The results from the lunar and exhaust samples confirmed the earlier analyses, and what appear to be free-base porphyrins were recovered from the products of MSA demetallation of both the lunar soil and the rocket exhaust. Results for extracts from both the sand and meteorite were negative.

The spectral characteristics and chemical behavior of the pigments in the lunar sample and the test rocket exhaust products are consistent with the identification of these pigments as porphyrins.

The porphyrins found in the lunar soil very likely were introduced by rocket exhaust. Thus, they possibly were generated in a new, high-temperature reaction involving very simple starting compounds.

10. ANALYSIS FOR METALLOPORPHYRINS BY MAGNETIC CIRCULAR DICHROISM *E. Bunnenberg and W. E. Reynolds*

The purpose of this investigation was to develop a sensitive nondestructive spectroscopic method, MCD, for the detection of metalloporphyrins in lunar extracts. MCD is a particularly useful technique for this purpose, since the observation of two S-shaped bands in the MCD spectrum of the lunar extract would provide more secure evidence for the presence of these compounds than is available from other spectroscopic techniques.

TECHNIQUE AND APPLICATION

Metalloporphyrins show three absorption bands in the 350- to 700-nm region. The positions of these three bands depend on the metal and on the ring substituents (ref. 27). Adopting the nomenclature of Platt (ref. 28), the transition of lowest energy (at about 570 nm) is designated Q_{0-0}; the transition Q_{0-1} at about 535 nm is a vibrational overtone of the 0–0 band; and the much more intense transition around 400 nm is designated B. The analytically important features in the MCD spectra of metalloporphyrins are the shapes of the MCD bands associated with the Q_{0-0} and the B transitions. The effective symmetry of metalloporphyrins is D_{4h}, and all bands are degenerate. In a magnetic field the degeneracy is lifted, and one observes the S-shaped MCD bands characteristic of A terms (ref. 29). The A terms associated with the Q_{0-0} and B bands are indicated in the MCD spectrum of Mg(II) deuteroporphyrins IX dimethyl ester shown in figure 17. Previous studies (ref. 30), as well as the reference spectra collected for this project (ref. 31), show that the magnitudes of the A terms of the B and Q_{0-0} bands are comparable, even though the absorption coefficients of these bands differ by an order of magnitude.

The MCD curve for Mg(II) deuteroporphyrins IX dimethyl ester was recorded under the experimental conditions used for the lunar sample measurement. Under conditions suitable for larger samples, the magnitudes of the A terms are more nearly comparable. Some metalloporphyrins (e.g., Cu(II) porphine), however, exhibit considerably more intense A terms in the B band than in the Q band. The utility of MCD for detecting small amounts of metalloporphyrins derives from (1) the intensity of the two prominent MCD bands, (2) their characteristic S shape, and (3) the observation of two such bands in particular regions of the spectrum.

Under the conditions used for these measurements, the detection limit relative to Mg (II) deuteroporphyrins IX dimethyl ester is 22 ng/ml. This limit is based on the condition imposed of observing both A terms. The detection limit based on observing the A term associated with the B band is 3 ng/ml. During these measurements, the detection limit in the Q region was degraded (1/3) by the necessity of using a wider than optimal slit width. If an A term had been detected in the B region, a noise-limiting circuit of the signal amplification system would have been energized. The slit width of the monochromator would have been reduced and the scan repeated. Under these conditions, the detection limit is 7 ng/ml (sample cell volume is 1 ml).

RESULTS

The MCD results obtained on the lunar extract sample are shown in figure 18. The instrument was adjusted to give the best possible solvent baseline (minimum slope) on October 7, 1969. The baseline was again measured on October 8, prior to the arrival of the lunar sample extract. This extract was placed in the cell and the MCD spectrum was recorded (fig. 18(a)) during an 80-min scan. The cell was emptied and filled with methanol. The baseline data obtained are shown in the computer plot presented in figure 18(b). It will be noted that neither the sample nor the baseline curve is flat. This feature is a characteristic of the particular photomultiplier tube used and does not degrade the information obtained. The raw data MCD curve of the sample corrected for solvent baseline is shown in figure 18(d).

The same procedure was followed for the sand blank sample. The MCD results are presented in figure 19. In the smoothed sand blank MCD curve shown in figure 19(d) it will be noted that the observed signal does not average about zero. This may have been caused by a very gradual movement of the arc during the time required to scan the sample and the solvent blank. However, the lunar extract MCD curve (fig. 19(d)) does not exhibit this feature.

DISCUSSION

The criteria established for the detection of a metalloporphyrin are (ref. 27):

1. The observation of an S-shaped A term around 570 nm. The long wavelength lobe will be negative with respect to the sign convention adopted.
2. The observation of a second S-shaped A term at about 400 nm. The long wavelength lobe of this A term will also be negative.

A critical examination of the MCD curve of the lunar extract shown in figure 19(d) reveals that:

1. The A term in the vicinity of 570 nm definitely is not present.
2. There is an *apparent* A term around 400 nm. As noted in a previous section, some metalloporphyrins exhibit a significantly more intense A term in the B band than in the Q band. However, the wavelength separation (23 nm) between the maximum of the negative lobe at 424 nm and the positive lobe at 401 nm is twice that observed in the reference metalloporphyrin spectra collected for this project. Furthermore, the approximately equal spacing between the positive and negative signals in the 335- to 475-nm region strongly suggests that these signals are actually instrumental artifacts.

On the basis of the criteria established, it is concluded that the amount of metalloporphyrins present in the lunar extract is less than 7 ng/ml.

ACKNOWLEDGMENTS

The MCD used in this project was built by G. H. Scott, Department of Chemistry, Stanford University. The computer interface was engineered by W. E. Reynolds (Genetics Department, Instrumentation Research Laboratory, Stanford University) with programming assistance from R. A. Stillman. Reference spectra measurements were made by R. Records.

11. AMINO ACIDS ASSOCIATED WITH PORPHYRINS

Gordon Hodgson and Berthold Halpern

Protein fragments may be associated with porphyrins in certain geological samples (ref. 32). Therefore, a search for amino acids associated with porphyrins was included in the lunar sample analysis scheme. In preparing for this work, it was found that through the application of spectrofluorometric techniques to dansyl derivatives of amino acids, small concentrations (~1 ng) of individual amino acids could be found. For the actual lunar analysis, however, this determination was not made because of the extremely low concentration of porphyrin detected ($\sim 10^{-4}$ μg/g). If amino acids were associated with this porphyrin, their concentration likely would have been below the limit of detection of the technique just proposed.

Amino acids in the benzene-methanol, H_2O, and 1N HCl extracts are discussed in Section 17.

12. ALKANES *Kathy Pering*

Because of their stability, alkanes are a common class of organic compounds in ancient rocks (ref. 33). The purpose of this work was to search for these molecules in the lunar sample.

METHOD AND MATERIALS

The benzene-methanol (9:1) extract of lunar sample (151 g) and sand blank (159 g) were evaporated on a rotary evaporator just to dryness in the 500-ml flasks in which they were received. The lunar extract was slightly opaque, and evaporation to dryness left a residue of black powder in the flask, but no free sulfur was visible. The flasks were rinsed twice with about 2 ml hexane. The hexane rinses were applied to two 9-mm, 9-g silica gel columns (Davison 923) and eluted with 15 ml hexane. The flasks were then rinsed twice with about 2 ml benzene. This rinse was applied to the columns and then eluted with 15 ml benzene. A final rinse of methanol was placed on the column and 15 ml methanol passed through. Copper strips were placed in the hexane fraction and allowed to stand for several hours. No tarnishing of the copper was observed, and it was concluded that no appreciable amount of free sulfur was present.

When the methanol fractions were evaporated down to about 3 ml, a fine, white, gel-like precipitate appeared. This has been observed before in other experiments and is attributed to dissolved silica gel from the column. The methanol fractions were transferred to 7-ml screwcap vials for fatty acid analysis. The benzene fractions were evaporated just to dryness and set aside for ultraviolet-visible spectroscopy.

The hexane fractions were evaporated to less than 1 ml and transferred to Pierce reaction flasks in 200-μl portions. Each portion was evaporated under a stream of nitrogen. The contents of the Pierce flasks were examined by gas-liquid chromatography (GLC) with a Perkin Elmer 880 gas chromatograph in a temperature-programmed analysis (2° C/min) on a 50-ft-long OV-1 Scot column. Under the chromatographic conditions used, pristane and n-C_{17} alkane were resolved, but phytane and n-C_{18} alkane were only partially resolved. After resolution and sensitivity were determined, a hexane blank was run (fig. 20), and 10% (2 μl) of the sand blank was examined (fig. 21). One peak was detected in the sand blank eluting from the column at 230° C. This peak was estimated to represent 0.09 μg (or 0.9 μg total) hydrocarbon. Peaks at this retention temperature have been seen before in extracts of the Pueblito de Allende meteorite and in its associated sand blank.

About 10% (2 μl) of the lunar sample was examined (fig. 22). A group of five partially resolved peaks appeared in the 210° to 240° C range and was estimated to represent 0.05 μg total (or 0.01 μg per peak) of hydrocarbon. Peaks of these retention times have occurred intermittently in our previous analyses of solvents. Although peaks of similar retention times were not observed in the sand blank, they should not necessarily be considered to be indigenous to the lunar sample. The peaks probably represent contamination. There was insufficient material in the sand blank to determine the structure of the single peak by combined GC/high-resolution MS.

CONCLUSIONS

The evidence above gives little indication that there are significant concentrations of alkane-like compounds in the lunar sample. Any isoprenoids or normal alkanes other than what might be in the group of peaks in the 210° to 230° C range must be present in concentration less than about 2×10^{-4} μg/g.

13. AROMATIC HYDROCARBONS *Etta Peterson*

The benzene fraction from silica gel chromatography was examined for the possible presence of aromatic hydrocarbons. These compounds, like the alkanes, are quite stable. The benzene fraction of the lunar sample and the corresponding benzene fraction from the sand blank were evaporated to dryness and dissolved in approximately 2 ml methanol. The absorption of the resulting methanol solutions was examined in the ultraviolet (from 350- to 200-nm) and the visible (700- to 350-nm) regions on the Cary 14 spectrophotometer.

In both samples, using the 0 to 1- and 1 to 2-OD slidewires, absorption was observed in the ultraviolet region (figs. 23 and 24). The main absorption occurred at wavelengths of 224, 274, and 280 nm. At these wavelengths, absorption was perhaps three to four times as intense in the lunar sample as in the sand blank. The visible region was featureless for both.

The similarity in the spectra of sample and blank suggests that the absorbing components in these samples possibly have a common source. Our interpretation is that the aromatic (i.e., ultraviolet-absorbing material) is not indigenous to the lunar sample.

14. FATTY ACIDS *Keith A. Kvenvolden*

Fatty acids are important biochemical compounds. They have sufficient stability to survive in many geological samples. Modern sediments contain both saturated and unsaturated fatty acids, but unsaturation disappears quickly with depth. Fatty acids are common in ancient sediments and have recently been reported to be present in Precambrian rocks (refs. 34 and 35).

In the analytical scheme devised for the lunar sample, fatty acids were sought in two places: (1) the methanol eluate from silica gel chromatography of the benzene-methanol extract (fig. 25), and (2) the BF_3-methanol extract obtained after the hydrolysis step with 6N HCl (fig. 26). Previous work on a recent sediment from Saanich Inlet showed that fatty acids were present in both of these extracts. The previous experiment set a precedent for applying the same analytical scheme to the lunar sample. Equivalent extracts from a sand blank were processed along with the lunar sample extracts in order to monitor possible laboratory contamination. The procedure described here applies to both the lunar sample and the sand blank.

METHOD AND MATERIALS

Methanol Eluate

About 15 ml of the methanol eluate from silica gel chromatography of the benzene-methanol extract of the lunar sample were concentrated on a rotary evaporator and transferred to a 2-dram vial with a teflon-lined screwcap. This solution was taken to dryness with a purified nitrogen stream on a bath maintained at 40° C. To the vial was added 1 ml of benzene and 3 ml of 14% BF_3 in methanol. The vial was capped and placed in a steambath at about 80° C for 10 min. The sample was allowed to cool. About 3 ml triple-distilled H_2O were added to the vial along with about 0.5 ml benzene. The vial was shaken and centrifuged at 1000 rpm for 3 min. The benzene layer separated and was recovered. The aqueous solution was extracted with 1 ml of benzene two times. The benzene solutions were composited in a 2-dram vial and taken to dryness using filtered nitrogen as described previously. For thin-layer chromatography, the contents of the vial were taken up in 100 μl of benzene.

BF_3-Methanol Extract

The BF_3-methanol extract solution, which weighed about 152 g, was concentrated to a volume of about 70 ml on a rotary evaporator using aspirator vacuum. This concentrate was transferred to a 250-ml separatory funnel. About 100 ml H_2O was added, and this mixture was extracted with 50 ml CCl_4 followed by two more extractions of 25 ml each CCl_4. The CCl_4 extract was concentrated on a rotary evaporator using aspirator vacuum to about 5 ml and was transferred to a 2-dram vial. This solution was evaporated using a nitrogen stream and a 40° C bath. The contents of the vial were dissolved in about 100 μl benzene for application on thin-layer chromatography plates.

Preparation for GLC

The 100-μl solutions derived from the methanol eluate and the BF_3-methanol extract were spotted on thin-layer chromatography plates (silica gel G without indicator, 20 X 20 cm, 0.25-mm thick, Brinkmann) along with standards containing methyl esters of n-C_{18} and n-C_{26} and hydrocarbon n-C_{22}. The plates were developed in a solution of hexane-diethyl ether-glacial acetic acid (90:10:1). When the solvent reached the top of the plate, the plates were dried and the region of the standards was visualized with 0.25% Rhodamine B spray reagent (Brinkmann). The bands corresponding to methyl esters and hydrocarbons were noted and removed from the plates. This silica gel and about 4 ml of benzene were placed in 15-ml centrifuge tubes having ground stoppers. The mixture was agitated on a Vortex mixer for 5 min and centrifuged for 3 min at 1000 rpm. The benzene was carefully pipetted from the silica gel. The gel was extracted a second time in the same manner with 3 ml benzene. The benzene solution was placed in 2-dram vials and evaporated to about 300 μl. This volume of liquid was transferred to small-volume, pointed reaction flasks and evaporated under filtered nitrogen at 40° C. To these flasks was added 20 μl n-hexane, and from this solution aliquots were taken for GLC.

ANALYSIS AND RESULTS

GLC was carried out on two flame-ionization instruments:

1. F&M 400; 6 ft X 1/4-in. glass column; 3% OV-17 on 60- to 80-mesh gas chrom Q; He flow, 50 ml/min; programmed from 100°–320° C at 5°/min; injection temperature, 200° C;

attenuation, 40 or 80; sample size, about 2 μl of 20 μl.

2. F&M 5754; 5 ft X 1/8-in. stainless steel column; 3% SE-30 on gas chrom Z; He flow, 20 ml/min; programmed from 118°–280° C at 4°/min; injection temperature, 220° C; attenuation, 20, 40, and 80; sample size, about 2 μl of 20 μl.

Two different instruments and columns were used to increase the confidence of any peak assignments that were to be made. The SE-30 chromatographic column resolved a homologous series of normal saturated fatty acid methyl esters, as well as $C_{16:0}$ from $C_{16:1}$ and $C_{18:0}$ from $C_{18:1}$ (fig. 27). The OV-17 column resolved only normal fatty acid methyl esters (fig. 28).

GLC revealed the presence of small concentration of fatty acids in both the lunar sample and the blanks. Table 14 summarizes these results. Figures 29 and 30 show the gas chromatograms from which the results were obtained. Unassigned peaks suggest the presence of compounds in the lunar sample that are not normal saturated fatty acids, but their identity could not be determined. Hydrocarbons could not be found in the BF_3-methanol extract.

DISCUSSION

The finding of small concentration of fatty acids in the lunar samples and the sand blanks strongly suggests that fatty acids were introduced in the laboratory during analysis. The fact that unsaturated fatty acids were found is good evidence that modern biological contamination cannot be clearly assigned to any particular reagent or procedure. It appears to result from airborne contamination of laboratory air. In the geochemical laboratories of UCLA, where different procedures are used, the same fatty acid contamination is present (J. W. Smith, personal communication). Careful evaluation of the GC data suggests that there are more compounds in the lunar sample than in the sand blank. However, the difference between the lunar sample chromatograms and the blank chromatograms is so small in most cases that little significance can be attached to it at this time.

The methanol fraction from the benzene-methanol extract did show about four peaks with retention times greater than *n*-C_{19} methyl ester. These peaks were not evident in the blanks. These compounds may indeed have been indigenous to the lunar sample, but their identity could not be established. If common fatty acids are present in the lunar samples at concentrations less than 10^{-2} μg/g, they would be masked by what appears to be a ubiquitous contamination.

15. FREE SUGARS FROM H_2O EXTRACTS *Sherwood Chang and JoAnn Williams*

The scheme adopted for the lunar sample analysis consists initially of separating the water into a neutral sugar-containing fraction and a basic amino acid-containing fraction with concurrent desalting by ion-exchange chromatography. Amino acids are converted to N-trifluoroacetyl *n*-butyl esters and analyzed by GC. (See Section 17.) In a portion of the neutral fraction, monosaccharides and other compounds containing hydroxyl or mercapto groups are converted to trimethylsilyl (TMS) ether derivatives for GC analysis. The presence of nonvolatile water-soluble aldehydes and ketones or other reducible compounds is detected by treatment of a second portion of the neutral fraction with sodium borohydride. The resulting reduction products, if derivatizable, are then converted to trifluoroacetates and analyzed by GC. If preliminary GC analysis of these portions indicates the presence of individual compounds in the total sample in excess of 100 ng, then the remaining extract is derivatized and these compounds analyzed by combined GC/MS. Structure indicated by GC/MS will be confirmed by comparison with authentic compounds.

EXPERIMENTAL

Apparatus

A Varian model 1520 GC with hydrogen flame detectors, modified for single-capillary column operation, was used for preliminary analysis. Combined GC/MS results were obtained using a Varian model 200 GC and CEC 21-110 high-resolution MS. A Rhyhage single-jet enricher served as the interface between GC and MS. Analyses of TMS derivatives of water-soluble neutral compounds were performed on a 5 ft X 0.02-in. neopentyl glycol adipate (NPGA), support-coated, open tubular column under the following conditions: helium flow, 5 ml/min; auxiliary helium flow, 20 ml/min; hydrogen flow, 25 ml/min; oxygen flow, 80 ml/min; initial column oven temperature, 180° C; initial isothermal period, 8 min, followed by program at 4°/min to 175° C where it is held; injection port temperature, 130° C; detector oven temperature, 200° C.

Chromatography of trifluoroacetyl (TFA) derivatives was accomplished on a 50-ft X 0.02-in. trifluoromethyl propyl silicone (FS-1265), support-coated, open tubular column under conditions described above for TMS derivatives, except that the initial column oven temperature was 140° C.

Reagents

All sugar standards were CalBiochem Grade A products. Standard TMS sugar derivatives were obtained from Pierce Chemicals, as was the Regisil reagent containing 1% trimethylchlorosilane. Methanol was a redistilled Baker-analyzed product. Trifluoroacetic acid and trifluoroacetic anhydride (TFAA) were purchased from Matheson Company and redistilled prior to use. Sodium borohydride was obtained from Alfa Inorganics. Water was triple distilled. All solvents and reagents were checked for substances that could interfere with GC analysis. Only in the case of TFAA was interference detected, and then only after the reagent was heated at 70° C for 5 min prior to GC analysis on the FS-1265 column. Redistillation did not eliminate all the contaminants. Materials from other suppliers (Peninsula Chem-Research and Distillation Products Industries) were no better. Thus, the impurities in heated TFAA stand as the minimum level of reagent contamination in the preparation of TFA derivatives.

Ion-Exchange Chromatography

Four small (9-mm-ID) glass columns equipped with teflon stopcocks were connected in series by teflon tubing and Luer-type adapters (fig. 31). Columns 1, 2, and 4 were packed with 1.5 ml of AG-50W-X8, 200- to 400-mesh resin in the hydrogen form. Column 3 contained 1.5 ml of AG-3-X4, 200 to 400 mesh, in the hydroxide form. All columns were regenerated six times prior to use. Stopcocks 1 and 4 were closed and stopcocks 2 and 3 were opened.

The aqueous blank extract (230 g) was colorless and clear, but the aqueous lunar sample extract (248 g) was cloudy, with a grey-brown irridescence indicating suspended particulate matter. Portions corresponding to 1.3% of the total blank and sample extracts (3.12 g and 3.18 g, respectively) were directly analyzed for amino acids by GC (see Section 17).

In 800-ml pear-shaped flasks, the lunar sample and blank extracts were each reduced in volume to about 1 ml on a Buchi rotary evaporator. A powdery grey-brown residue appeared in the sample extract but the blank remained clear. The sample extract was transferred to a teflon-capped tube, shaken in a sonicator for 1 min, and spun at 4000 rpm in an International centrifuge. Column 1 was disconnected from column 2, and the clear solution from the sample placed on the bed of column 2. The original flask was rinsed with 0.5 ml water and the water transferred to the

centrifuge tube containing the residue, which was sonicated for 1 min, followed by centrifugation as before. The liquid was again placed on column 2. This rinse procedure was repeated and the final residue stored for safekeeping. The solution on top of column 2 was slowly run just to the top of the resin bed by opening the bottom stopcock. About 0.5 ml water was added to the top of column 2. Column 1 was reconnected to column 2 and stopcock 1 was opened. From the end of column 4, 14.5 g of eluate was collected in a 50-ml pear-shaped flask.

This colorless eluate was reduced to 0.25 g on a rotary evaporator, then distributed to three Pierce Reactivials in the proportion 1:2:3, labeled LSA_1, LSA, LSB. Column 2 was disconnected from the assembly and eluted with 2N ammonium hydroxide. The resulting 9.8 g of basic solution was reduced in volume to 0.16 g and stored at 8° C to await derivatization for amino acid analysis (Section 17). Column 3 was disconnected from the assembly and eluted with 1N HCl. The resulting 11.1 g of acidic solution was saved for sulfate determinations.

The ion-exchange columns were regenerated twice and reassembled in series as before. The blank extract was then reduced in volume and submitted to the centrifugation and ion-exchange procedure used for the lunar sample. The neutral eluate was reduced to 0.17 g and distributed to three Reactivials in the proportions 1:2:3, labeled as LBA_1, LBA, LBB. The 10.5 g of basic eluate from column 2 was reduced to 0.20 g and stored for later amino acid analysis. The 10.0 g of acidic eluate from column 3 was saved for sulfate determinations.

Trimethylsilylation of LSA_1 and LBA_1

Sample LSA_1 and blank LBA_1 were freeze-dried, leaving minute amounts of whitish residue in both vials. To each was added 10 μl of acetonitrile-Regisil solution (10:1 by volume). After heating in the sealed vials at 70° C for 10 min, the vials were cooled to room temperature and 4-μl aliquots of the solutions analyzed on the NPGA column. This injection volume corresponded to 7% of the total sample and blank extracts.

Reduction and Trifluoroacetylation of LSB and LBB

Sample LSB and blank LBB were freeze-dried, again leaving a faint white residue. To the vials were added 25 μl of an aqueous solution of sodium borohydride (4 mg in 2 ml of water). Gas evolution, which took place in both vials, rapidly subsided in the blank LBB, but continued in the sample LSB during 3 hr at room temperature with frequent agitation. Excess borohydride in LSB and LBB was decomposed with a drop of trifluoroacetic acid. The resulting sodium trifluoroacetate serves as catalyst for the trifluoroacetylation reaction. The two acidic solutions were taken to dryness in a stream of dry, filtered nitrogen on an aluminum block heated at 60° C. Two drops of methanol were added to each vial and the vials heated at 60° C for 2 min. The methanol was evaporated with a stream of nitrogen. This procedure was repeated five times to remove borate ion as methyl borate, thereby eliminating borate interference in the subsequent trifluoroacetylation. Twenty-five microliters of TFAA were added to each vial and the capped vials heated at 70° C for 50 min. After cooling, 2.5 μl of each solution were injected on the FS-1265 column. This injection volume corresponded to 5% of the total water and blank extracts.

The reduction and trifluoroacetylation of LSA and LBA were carried out in the same fashion.

Control Experiments: Recovery of Monosaccharides and Establishment of Minimum Detectable Limits

Ten microliters of freshly prepared solution containing 40 ng each of ribose, arabinose, and glucose per microliter were diluted to 225 ml with water. Using the procedure outlined earlier for ion-exchange chromatography, this solution was evaporated and chromatographed. The neutral eluate was taken to dryness, reduced with sodium borohydride, and treated with TFAA as described above. The TFAA mixture was reduced to about 5 μl and the entire sample injected on the FS-1265 column. At an electrometer attenuator setting of 1.6, the resulting pentitol derivatives registered 75% of full scale (fig. 32). In another experiment, the sugars contained in 10 μl standard solution were reduced and derivatives obtained without the dilution and ion-exchange steps. Injection of two-thirds of the total samples registered 50% full recorder scale for pentitol derivatives and 40% for the hexitol derivative (fig. 33). The results indicate that recovery of submicrogram amounts of monosaccharides after evaporation of extracts and ion-exchange chromatography is essentially quantitative. Furthermore, reduction and trifluoroacetylation occur in sufficient yields to permit detection of monosaccharides as the sugar alcohol derivatives in nanogram quantities. At the electrometer attenuator setting of 0.4 used in the analyses, as little as 3 ng of extracted monosaccharide could be detected.

The chromatograms in figure 34 show the products and detector responses obtained from derivatization of an equivalent of 100 ng of each of seven monosaccharides in a mixture (arabinose, ribose, lyxose, mannose, galactose, and glucose) according to the procedure given for the trimethylsilylation of LSA_1 and LBA_1. Comparison of total response for all peaks at the electrometer attenuator setting of 0.8 with the amount of monosaccharides initially present indicates that as little as 2 ng of an individual compound can be detected.

Performance blanks were run in parallel with each derivatization of lunar sample and sand blank extracts. These involved placing in a separate vial a volume of pure water equal to the volume of lunar extract being derivatized. The contents of the vial were then treated in an identical fashion as the lunar sample and associated sand blank. GC analysis of the performance blanks reveals any contamination introduced through solvents, reagents, or handling during the derivatization process.

RESULTS

During trimethylsilylation, individual sugars always gave at least two derivative GC peaks due to formation of anomeric pyranosyl and/or furanosyl isomers during derivatization. Use of pyridine as solvent and hexamethyldisilizane and trimethylchlorosilane as derivatizing agents eliminates this problem; however, it creates a much more serious tailing problem during GC analysis, which completely prevents submicrogram-order analyses for monosaccharides. Nevertheless, formation of multiple peaks for monosaccharides has its advantages, because it can be concluded that any single peak appearing in a chromatogram over an established range of retention temperatures cannot correspond to a pentose or hexose but must be a member of some other class of compounds containing an active hydrogen.

The indicated trifluoroacetylation conditions produce several minor unidentified products (figs. 32 and 33) that increase in relative amounts over a period of several days. These are probably partially derivatized sugar alcohols formed during the reaction or by subsequent decomposition.

Chromatograms for a performance blank, lunar sample LSA (17% of total neutral fraction), and associated sand blank LSA after trimethylsilylation are reproduced in figure 35. The injection

volumes correspond to 7% of the total neutral fraction. No discrete peaks were found in the performance blank between retention temperatures 150° and 185° C, indicating the absence of contamination in this region during derivatization. Irregularities in the chromatogram appear in 185° C isothermal region and may be attributable to contaminants. These constitute the irreducible background. In the lunar sample chromatogram (fig. 35), a maximum of nine discernable peaks appear. Except for peaks 1 and 2, which elute before pentose TMS derivatives, the rest occur in the sand blank, and peaks corresponding to 4 to 7 are also found in the performance blank. Without knowing the identities of materials in peaks 1 and 2, no quantitative estimate can be made of their abundance in the sample. If we assume they are TMS derivatives of sugar-like (polyhydroxy) substances, a rough estimate of less than 50 ng of total extractable and derivatizable material can be made. Clearly, no pentose or hexose derivatives were detectable in the lunar sample. Thus, less than 30 ng ($< 10^{-3}$ μg/g) of extractable monosaccharide were present in the sample. The sensitivity of the GS analysis is illustrated in figure 36, in which peaks 1, 2, and 3 correspond to 3 ng each of α-D-arabinose, α-D-xylose, and β-D-glucose, respectively, as the TMS derivatives.

With hopes of detecting water-soluble compounds containing functional groups reducible to hydroxyl, mercapto, or amino functions, lunar sample LSB (50% of total neutral fraction) and the associated sand blank LBB were reduced with sodium borohydride and derivatized with TFAA. The reduction of both resulted in noticeable initial gas evolution, which in the case of LSB, continued for 3 hr. No gases were observed with a performance blank, which had been processed from initial dilution with 225 ml water through ion-exchange chromatography to reduction, or in the control experiments where 400 ng of several monosaccharides were put through the analysis scheme and reduction procedure. Apparently, substantial reducible material occurred in both the lunar sample LSB and the sand blank LBB, with a larger amount in the former. As shown below, however, very little reduced product could be detected, far less than expected for the amount of gas evolved. Possibly the reaction involved water-soluble polymeric material that contained a variety of reducible groups. In this case, treatment with sodium borohydride would result in gas evolution, but the reduced product would retain its polymeric nature and not be volatilized during derivatization and GC analysis. Or, if reduction of polymer resulted in very small fragments, these would be lost in the solvent peak of GC. Of course, a combination of these two processes is possible.

Chromatograms of the performance blank, lunar sample LSB, the associated sand blank LBB, and a standard containing 50-ng equivalents of five sugar alcohols (ribitol, arabitol, xylitol, mannitol, and sorbitol) are reproduced in figure 37. Injection volumes in the first three cases correspond to 5% of the total neutral fraction. The small peaks in the performance blank (fig. 37(c)) constitute the irreducible background. Under GC conditions, derivatives of hydroxy compounds as small as glycerol and as large as a heptitol are conveniently eluted. In the lunar sample LSB (fig. 37(b)) there are eight significant peaks, of which only peaks 3, 4, 5, and 7 are not in the sand blank LBB (fig. 37(c)). Of these four, peak 5 contained sufficient material to warrant derivatization of the remaining lunar sample LSA and pooling with LSB. Assuming detector response similar to that of a pentitol trifluoroacetate, about 100 ng of material would be available for GC/MS. Substances in the remaining peaks correspond to less than 30 ng per peak in the entire neutral fraction of the water extract and were not investigated further.

Chromatograms of lunar sample LSA (33% of total neutral fraction) and associated sand blank LBA are shown in figure 37(e, f), respectively. In these runs, the initial GC oven temperature was lowered to 125° C, but the temperature program rate remained unchanged. The substance that

corresponds to peak 5 in LSB appears as a shoulder on peak 6 in LSA. The latter peak did not show up in LSB and may have been introduced during derivatization. Interference from peak 6 precluded pooling LSA with LSB. The remainder of LSB was analyzed by GC/MS, but no response was recorded on the ion-beam monitor. Samples LSA, LBA, and LBB were combined and run on GC/MS. The resulting ion-beam monitor trace showed two peaks corresponding to peaks 6 and 7 in LSA and LBA (the latter having as its counterpart peak 6 in LBB). Both peaks apparently are not indigenous to the lunar sample. No data were obtained from the photoplate readout and computer output.

CONCLUSIONS

1. Control experiments show that submicrogram quantities of extractable monosaccharides can be recovered quantitatively during analysis. A detection limit for the entire lunar sample can be set at 30 ng of a single monosaccharide as the TMS derivative.
2. Fifty grams of lunar sample contained less that 39 ng of pentose or hexose monosaccharides and less than 50 ng of other directly derivatizable compounds.
3. Substantial material reducible by sodium borohydride was present; however, only four trifluoroacetylated reduction products were detectable. Three amounted to 30 ng each, the fourth less than 120 ng—too little in all cases for identification by GC/MS.

16. NUCLEIC ACID BASES FROM 1N HCl EXTRACTS *Carl Saxinger*

Nucleic acid bases were sought in the lunar sample analysis because of their importance to living systems on earth. Refluxing of the lunar fines for 1 hr with 1N HCl should hydrolyze the nucleic acid bases without appreciably altering their structure.

About 90% of the 1N HCl hydrolysate was filtered through a 6-mm column containing about 500 mg of a 1:1 mixture of Norit A charcoal (Nutritional Biochemical Corp.) and Celite 545 (Johns-Manville). This mixture had been prepared previously by refluxing with a sequence of solvents: 2N HCl, 6N NH_4OH, pyridine-water (1:1), pyridine, water, methanol, a mixture of benzene-ethanol-water, benzene, formic acid, and water. The filtration removed purines, pyrimidines, and other nonpolar hydrophobic and aromatic molecules. The filter was washed with 50 ml 1N HCl and 50 ml water to remove loosely adsorbed material, e.g., amino acids, sugars, and salts. The charcoal mixture was extracted with formic acid for 5 hr at 40° C and the extract evaporated to dryness in a 40° C bath. The last traces of formic acid were removed by NaOH pellets in a dessicator. The charcoal elution procedure was followed closely to ensure quantitative elution without extraction of background contaminants from charcoal. A portion of the residue was reacted with bis(trimethylsilyl)trifluoracetamide (ref. 36) to make TMS derivatives of any purines and pyrimidines that might have been present. The derivatized mixture was analyzed by GLC.

The analytical scheme is outlined in figure 38. GC was performed on an F&M Model 400 GC with a 6 ft X 1/4-in. glass column packed with 3% OV-17 on 60- to 80-mesh Chromasorb Q. For each chromatogram the temperature was held at 100° C for about 6 min and then increased at the rate of 7.5°/min to 300° C. Figure 39 is a gas chromatogram showing 0.75 nmol each of seven derivatized nucleic acid bases. The performance background is shown in figure 40. The extract here was obtained by following the scheme of analysis using the solvents, reagents, and charcoal only, without the sample. Figure 41 shows the gas chromatogram obtained from the sand blank.

The source of the peaks is unknown, for these same peaks were not observed in the chromatogram of the lunar sample (fig. 42). The material in the lunar sample proved to have only limited stability because the chromatogram could not be repeated after 10 days.

A 3-ml sample of HCl-free, charcoal filtrate was subjected to cation-exchange chromatography using Dowex 50 (NH_4^+) by the batch technique. Trimethylsilylation followed by GC of the derivatives produced no peaks.

Approximately 2 ml of 1N HCl hydrolysate and 6 ml of the charcoal-filtered 1N HCl hydrolysate from the lunar sample were analyzed by GC of the solution resulting from N-TFA *n*-butyl derivatization (Section 17).

Direct-probe analysis by MS (CEC 21-110) was done at 7.5% of the prepared extracts. The purpose was to determine the presence of heterocyclic-base ion fragments. Results obtained from mass spectra are inconclusive. Reflected light photographs indicate presence of rhombic crystal, suggesting sulfur.

Common nucleic acid bases were not detected; at present, it must be concluded that, if present, they must amount to less than roughly 4×10^{-3} μg/g. Since it is expected that charcoal adsorption and elution as used here would isolate a large number of classes of aromatic heterocyclic bases, the material seen in the lunar sample could possibly be of interest. The lunar material was eluted at a temperature just slightly above the elution temperature of guanine. Although the material displayed reproducible GC behavior over a period of several days, total detectable activity was lost by the time MS was about to be attempted—a period of 7 to 10 days.

17. AMINO ACIDS FROM EXTRACTS AND HYDROLYSATES

Charles Gehrke, David Stalling, Walter Ave, and Robert Zummalt

Use of GLC techniques for the analysis of amino acids as their N-TFA *n*-butyl esters permits the detection of nanogram quantities of these compounds in geologic samples. The procedure outlined here for the analysis of amino acids in the lunar sample evolved from the application of this technique to modern sediments from Saanich Inlet, British Columbia; a basalt from Hawaii; and a sample of the Pueblito de Allende meteorite. Analysis for amino acids in the lunar sample was conducted on preparations from various stages in the extraction and separation scheme used by the consortium (fig. 1). These preparations included: (1) benzene-methanol extract, (2) H_2O extract, (3) 1N HCl extract, and (4) 6N HCl hydrolysate.

EXPERIMENTS AND RESULTS

All samples were analyzed on 1.5-m X 4-mm glass columns; one containing 0.325% EGA on 80- to 100-mesh AW Chromasorb G, the other containing 3.0% OV-17 on 80- to 100-mesh HP Chromasorb W. Complete performance blanks were run for every analysis performed.

Benzene-Methanol Extract

During the lunar sample analysis and evaluation of methods, it was found that any free amino acids present in nanogram concentration in a mineral matrix will be extracted in the presence of excess benzene-methanol (9:1). One gram of lunar sample was extracted excessively with benzene-methanol, taken to dryness, and then derivatized to make the N-TFA *n*-butyl esters (refs. 36–38) of any amino acids that might be present. Examination of the resulting mixture by GC on the EGA column revealed no significant chromatographic peaks corresponding to the common amino acids.

Only one small peak was observed at a concentration no greater than 10^{-1} μg/g (fig. 43). It is concluded that amino acids were not present in the sample at concentrations greater than 10^{-2} μg/g.

H_2O Extract (see Sections 8 and 15 for preparation of extract)

GLC analysis (fig. 44(a)) of the water extract that had not been passed through an ion-exchange column revealed three minor chromatographic peaks, which do not coincide with the common amino acids. The concentrations of these peaks were too low to be suitable for GC/MS analysis.

GLC analysis of the desalted sample (NH_4OH eluate from Dowex 50 column) revealed the absence of any significant chromatographic peaks (fig. 44(b)). The sample was extremely clean, indicating that the small peaks observed on analysis of the untreated water extract (fig. 44(a)) were not retained on the desalting column and, therefore, were not amino functional. Figure 44(c,d) also shows typical sand blank and sensitivity analyses.

HCl Hydrolysates

1N HCl (see Sections 8 and 16 for preparation of extract). This hydrolysate was analyzed before and after it was passed through a charcoal column adsorption designed to remove nucleic acid bases. Both samples gave essentially identical chromatograms (fig. 45(a)), indicating that none of the compounds with observed peaks was adsorbed on the charcoal. Five significant peaks were observed whose retention times did not correspond to any of the common amino acids; these also did not appear in the sand blank.

The materials represented by the GLC peaks could not be held on a cation-exchange column, confirming the absence of amino functional groups.

On the other hand, the unknown materials apparently need both esterification and acylation in order to allow successful chromatography and, therefore, must be bifunctional. This was proven by the analysis of three different samples: (1) an esterified and acylated sample (fig. 40(a)), (2) an acylated sample (fig. 40(b)), and (3) an esterified sample (fig. 40(c)). A performance standard is shown in figure 40(d).

After the esterification and acylation reactions (fig. 40(a)), strong peaks in the 100- to 300-ng range from an equivalent of 3.7 mg of lunar material injected were observed. To extend the range of analysis and provide a more inert separation medium, an OV-17 column was used to confirm the presence of the compounds in the lunar material. More peaks than those found with the EGA column were discovered (fig. 46(a,b)). Figure 46(c) is a performance standard on the OV-17 column. These peaks do not show up when the polyester liquid phase is used because of decomposition of compounds on the column. Similar behavior has been observed earlier with several amino acids and other compounds that are difficult to chromatograph on the polar EGA liquid phase.

Neither the chromatogram of the 1N HCl hydrolysate of the sand blank (fig. 46) nor the chromatogram obtained from 1N HCl hydrolysis of materials from trap E of the rocket exhaust test (ref. 26) (fig. 47) showed any of the peaks found in the lunar sample.

A specially concentrated lunar sample was chromatographed on a GLC unit coupled to a MS. Both EGA and OV-17 columns were used, and the mass spectrum of each emerging peak recorded on a photoplate. From a 3-μl injection, the amount of substance (represented by the largest peak) that reached the MS after chromatographic separation and molecular separation was estimated from the beam monitor response as ~0.5 μg. Assuming a molecular separator efficiency of 20%, ±2.5 μg of lunar material was injected. An estimate of the total amount lunar substances found

as peaks in the chromatograms would be somewhat below 0.01% of the original lunar material. Interpretation of photoplates was equivocal.

6N HCl (see Sections 8 and 18 for preparation of extract). On GLC analysis of the 6N HCl hydrolysate, no common amino acids were found (fig. 48). However, two chromatographic peaks were observed during this analysis on an EGA column that eluted at 113° and 138° C. As these peaks represent derivatives of unknown compounds and are found in greater concentrations in the 1N HCl extract, the latter accounted for the major part of the reported investigations.

Results. The 1N HCl and 6N HCl hydrolysates of the lunar sample (10086,3) contain appreciable amounts of derivatizable material, which has been analyzed by GS/MS techniques. This material contains compounds that were absent in both the sand blank and the rocket exhaust blank and do not correspond to any of the common amino acids. These compounds were not present in the benzene-methanol extract or in the water extract of the lunar sample.

Therefore, it is concluded that, if common amino acids are present, they must be in concentrations less than 2×10^{-3} μg/g. Five significant chromatographic peaks were obtained only in the lunar sample and did not appear to be artifacts of the derivatization procedure. The combined concentration represents 20 to 35 μg/g of organic compounds (calculated on the same response basis as amino acid derivatives) or 10 to 20 ppm carbon. The peaks could not be observed without esterification and acylation.

ADDITIONAL EXPERIMENTS AND CONTROLS

Because the initial analysis yielded positive results, the analysis was repeated with additional control samples examined to increase confidence. The following is an outline of the experiments conducted in conjunction with this analysis as well as the analysis of the lunar sample itself.

Reagents and Chromatographic Blank

All chemical reagents, sand blank (1N HCl hydrolysis of quartz sand at 100° C for 1 hr), and GLC column blanks were run and found to be free of contaminants at a level of 0.05 ppm (fig. 49(a–d)). Figure 49(e) is a sensitivity check.

Organic Reaction Derivatization Standard

The chemistry of the derivatization method used was checked by analyzing a five-component sample containing different functional groups. The molecules were: 1-octanol, 1-amino hexane, valine, lauric acid, and adipic acid. All these compounds were derivatized quantitatively as the *n*-butyl ester or O,N-TFA *n*-butyl ester (refs. 37–39) and successfully chromatographed on a 1-m column of OV-17, 1.5 w/w% on high-performance, 80- to 100-mesh Chromasorb G (fig. 50(a)).

Recovery of Standard Mixture

The five-component standard mixture described in reference 36 was added to an aliquot of the 1N HCl hydrolysate of the lunar sample and derivatives obtained. Recovery of four of the five molecules was achieved at a level of 80%; adipic acid was not recovered (fig. 50(b)).

Amino Acid Standards, GLC/MS

Four different amino acids with different functional groups were analyzed by GLC/MS at concentrations of 500 ng, 5 μg, and 25 μg of each per 5 μl. Final acylation volume was 500 μl, and 5 μl were injected into the GC. The amino acids were leucine, proline, aspartic acid, and lysine. It

was the purpose of this experiment to determine the minimal detectable amount and linearity of abundance ratios of ion fragments by GLC/high-resolution MS. Initial computer dumps showed that no spectra were obtained when 500 ng were injected into GLC/MS (fig. 51(a,b)).

1N HCl Hydrolysate of Lunar and Pueblito de Allende Meteorite Samples

Two grams of lunar sample and meteorite were hydrolyzed at reflux with an 4:1 (v:w) of 1N HCl for 1 hr. Direct injection of the derivatized samples into the GC showed that the lunar and meteorite samples contained organic compounds with similar retention temperatures. The GLC chromatograms were similar and showed at least five major peaks and a number of minor peaks (fig. 52(a,b)).

Pentane Extraction of Derivatized Molecules

After derivatization of the 1N and 6N HCl hydrolysates obtained from a carbide experiment (Section 3) on the lunar sample and the 1N HCl hydrolysate of the meteorite sample, the samples were extracted with 200 to 500 μl pentane to remove the derivatized molecules from the large amount of salts in the microreaction vial.

The gas-liquid chromatograms for the lunar and meteorite samples were strikingly similar (fig. 53(a,b)). Control chromatograms are shown in figure 53(c–e).

Concentration of Organic Compounds

The concentration of organic compounds derivatized by esterification and acylation in the 1N and 6N HCl hydrolysates of the lunar sample is at least 20 μg/g, with one additional compound at the 20- to 30-μg/g level. This latter compound was not in the blanks and is not well resolved from the solvent peak. Thus, the total organic matter could easily be 40 to 50 ppm. The concentration of organic compounds in the meteorite is about 45 to 60 ppm.

Direct-Probe Mass Spectrometry

Samples of the 1N HCl hydrolysates of the sand blank and meteorite and lunar materials were derivatized and analyzed by direct-probe MS (CEC 21-110).

Also, underivatized samples of the 1N HCl hydrolysates of the meteorite and lunar samples were analyzed by direct-probe MS to confirm the presence or absence of silicon and organic material in the extracts.

Rocket Exhaust, Basalt, and Quartz Crystals

Acid hydrolysates (1N HCl) were made of the lunar rocket exhaust (trap A) (ref. 3) and Hawaiian basalt, and a 6N HCl hydrolysate was made of pulverized quartz crystals from Africa.

Trap A showed two major and four minor peaks on GLC. Two of these peaks have a retention time similar to that of the peaks found in the meteorite and lunar samples. However, the possibility of contamination of the meteorite sample by rocket exhaust is not likely. A concentration of 5000 ppm organic material was found in the residue remaining after benzene-CH_3OH extraction of trap A (fig. 54). Three parts per million organic material was found in the basalt sample, and 0.3 ppm in the quartz crystals (fig. 55(a–c)). Figure 55(d) shows a sensitivity check. Neither of these materials was chromatographically similar to the lunar or meteorite samples.

Results

Organic compounds were found in the 1N HCl hydrolysates of the lunar and meteorite samples. These peaks could not be observed without conducting both esterification and acylation.

1. The total concentration of these organic components is 35 to 50 ppm in the lunar sample and 45 to 60 μg/g in the meteorite sample. The gas-liquid chromatograms were strikingly similar, showing the same major peaks.
2. These results indicate that the following functional groups may be present: carboxylic or cyano, and hydroxy, amino, imino, and sulfhydryl.
3. Neither the calcined sand blank nor the trap E material from rocket exhaust tests showed any of the peaks found in the lunar or meteorite samples. Further, the peaks observed for rocket exhaust (trap A) did not coincide, with one exception, with those for the lunar or meteorite samples.
4. Mass spectrometry of major compounds observed in lunar and meteorite samples suggested that these compounds are organosiloxanes.

18. AMINO ACIDS FROM 6N HCl HYDROLYSATES *Jessi Flores and Jerri Mazzurco*

The scheme of analysis was designed so that if bound amino acids were present in the lunar sample, the bulk would be obtained in the 6N HCl hydrolysate. The 207 g of blue-green 6N HCl hydrolysate from the lunar sample was split into fractions A and B with net weights of 98 g and 109 g, respectively. Ten milliliters from fraction A were weighed in a 10-ml volumetric flask for density determinations, yielding D = 1.15 g/ml. From this density, the equivalent weight of lunar material per milliliter 6N HCl hydrolysate was calculated at 0.303 g/ml. The 10 ml derived from fraction A were evaporated to dryness and redissolved in 6 ml H_2O, which gave a concentration of 0.5 g lunar material per ml H_2O. Two milliliters (1 g) were taken for further work, and the balance of 4 ml (2 g) was taken for GC analysis (Section 17).

The 1-g equivalent of lunar extract was evaporated to dryness, redissolved in H_2O, charged on a 10-ml Dowex 50 (H+ form), and eluted with four-bed volumes of H_2O. Two-bed volumes of NH_4OH were then collected. The NH_4OH eluate, presumably containing the amino acids, was evaporated to dryness. A white residue formed that was insoluble in water added to dissolve any amino acids present. The water solution was decanted from the white residue and charged on the amino acid analyzer (Beckman 120C).

The amino acid analyzer results from the 1-g sample are shown in figure 56(a). Peaks corresponding to the following amino acids were found: serine, 0.08 nm; glycine, 0.1 nm; and alanine, 0.1 nm. The possible presence of serine suggested contamination. Therefore a check was made by rerunning 1 g (3.3 ml) of fraction A. The results are given in figure 56(b). Peaks corresponding to the following were found: glycine, ~0.08 nm; alanine, recorder problems; and serine, absent.

The equivalent of 5 g of lunar sand blank also was analyzed. The results (fig. 56(c)) showed no evidence for amino acids except perhaps about 0.08 nm glycine. The small amounts of possible glycine and alanine are probably not indigenous to the lunar material. A number of solvent blank runs passed through Dowex 50 consistently gave small amounts ($\leq$ 0.01 nm) of glycine and alanine. No common amino acids were found by GLC (Section 17) at concentrations of 2×10^{-3} μg/g. However, two GLC peaks were found at the 5- to 10-μg/g level that were similar in retention time to those peaks observed in the 1N HCl hydrolysate from the first analysis of the lunar sample.

19. GASES EVOLVED DURING HYDROLYSIS *Ian Kaplan and John W. Smith*

The gases evolved during hydrolysis of the lunar sample were collected for isotopic composition studies. The venting system designed to collect these gases is shown in figure 7. Hydrogen sulfide was removed by precipitation in a 10% silver nitrate solution, and carbon dioxide was to be frozen out in liquid nitrogen. The precipitated silver sulfide was collected on a preweighed Millipore filter, and thoroughly washed with 1:1 ammonium hydroxide solution and finally with water. The sulfide was dried at 105° C, weighed, and quantitatively converted to sulfur dioxide for MS analysis (ref. 2). The concentration of sulfides in the sample was about 700 μg/g with an average $\delta^{34}S$ of +8.0 (relative to Canyon Diablo meteorite). See Section 4 for a discussion of sulfur isotopic compositions.

Some nitrogen may have condensed in the liquid nitrogen trap during the hydrolysis experiment. This gas was slowly removed by evaporation at liquid nitrogen temperatures. The volume of the residual condensed gases was measured manometrically at the ambient temperature. No carbon dioxide was detected. The condensation of nitrogen within this trap and its subsequent evaporation may have resulted in the loss of small volumes of carbon dioxide if present. This method of trapping, therefore, does not appear to be useful in situations where only traces of carbon dioxide may be released during acidification. Further experiments revealed only traces of carbon dioxide (>5 μg/g).

CONCLUSIONS

1. Indigenous carbon is present at concentration of about 150 μg/g in a sample of lunar dust from Mare Tranquillitatis (Apollo 11 mission).
2. Acid hydrolysis of the lunar sample at 100° C yields C_1 through C_3 and possibly C_4 hydrocarbons. This result suggests the possible presence of carbides that have generated hydrocarbons during attack by HCl. At least 20 μg/g of carbon in the lunar sample can be accounted for in the experiment.
3. Carbon monoxide and carbon dioxide were present as products of pyrolysis. Carbon in concentrations ranging from 50 to 120 μg/g can be accounted for in the pyrolysis products.
4. Compounds derivable as N-TFA *n*-butyl esters were found mainly in the 1N HCl hydrolysate. Their combined concentration amounted to about 35 to 50 μg/g, calculated on the same response basis as amino acid derivatives. The compounds in the hydrolysate, however, were not amino acids. Some of the compounds were identified as organosiloxanes.
5. Compounds whose fluorometric spectral response suggests porphyrins are present in concentrations of 1×10^{-4} μg/g. Pigments with similar spectral responses also were found in tests of rocket exhaust products. The material of the lunar sample may have been introduced by the lunar descent rocket engine at the lunar surface.
6. The isotopic compositions of carbon and sulfide sulfur in the lunar sample are significantly different from compositions determined for other extraterrestrial samples.
   a. The carbon isotopic composition of the total carbon is $\delta^{13}C = +20$ (relative to PDB standard). Noncarbonate carbon of meteorites ranges from about −4 to −30. The lunar sample had no detectable carbonate carbon; therefore, the bulk of carbon is noncarbonate, and its $\delta^{13}C$ composition lies outside the range of values found previously in extraterrestrial samples.
   b. The isotopic composition of the sulfide present in concentration of about 700 μg/g is $\delta^{34}S = +8.2$ (relative to Canyon Diablo standard). $\delta^{34}S$ of meteorites range from +2 to −2.
7. Hydrocarbons, fatty acids, amino acids, sugars, and nucleic acid bases, if present in this lunar sample, are below present levels of detection, which vary from 10^{-5} to 10^{-2} μg/g, depending on the class of compound being examined.
8. These findings are specific for a surface sample from Mare Tranquillitatis. Samples from other sites may be expected to yield widely differing results.

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Table 1 Total Weights of Lunar Material Taken for Experiments

Experiments	*Grams*
Mass spectrometry	0.0212
Organic carbon	0.0614
Total carbon (includes isotopes, carbide, and pyrolysis determinations)	23.2
Microfossils	2.0
Mineralogy	0.250
Extraction	
Bulk sample	54.6
Porphyrin repeat	10.1
Derivatization experiments	4.1
Total	93.9

Table 2 Mass Spectrometry — Ion Fragments

C_2H_5N	C_3H_5NO	$C_2H_5N_2O$
C_2H_6N	C_4H_5NO	$C_3H_5N_2O$
C_3H_4N	C_5H_4NO	$C_3H_6N_2O$
C_3H_5N	C_5H_5NO	$C_5H_6N_2O$
C_3H_6N		$C_5H_7N_2O$
C_3H_7N		$C_5H_8N_2O$
C_4H_4N		$C_6H_8N_2O$
C_4H_5N		$C_7H_9N_2O$
C_4H_6N		
C_4H_7N		
C_4H_8N		$C_4H_4O_2$
C_4H_9N		C_6H_5O
C_5H_7N		$C_5H_6O_2$
C_5H_8N		$C_4H_8O_3$
C_5H_9N		$C_6H_5O_2$
$C_5H_{10}N$		$C_5H_7O_3$
$C_5H_{12}N$		$C_5H_9O_3$
C_6H_6N		$C_7H_5O_2$
C_6H_8N		
C_8H_7N		
	$C_4H_6O_2N_2$	

Table 3 Organic Carbon Determinations

I	Freshly incinerated ground sand blank			0.6 μg/g
II	Sand control (ARC-4)	17.0 ± 3.4		
		2.5 ± 1.6		
		0.9 ± 1.4		
		−0.6 ± 1.2		
			average	4.9 ± 6.5
III	Pueblito de Allende (NASA 31-4A)	15.5 ± 3.3		
		17.1 ± 3.5		
		15.2 ± 3.3		
		9.7 ± 2.6		
			average	14.4 ± 3.2
IV	Lunar sample 10086 Bulk A Fine (ARC-4)	38.6 ± 8.2		
		40.4 ± 8.5		
			average	39.5 ± 8.3

Note: Samples II, III, and IV have had the 0.6-μg/g blank subtracted to give the above figures.

Table 4 Amounts of Carbon (μg/g) Produced as Hydrocarbons During Hydrochloric Acid Hydrolysis of Lunar and Meteorite Samples

	Experiment	CH_4	C_2H_4	C_2H_2	C_2H_6	C_3H_6	C_3H_8	*Other* C_3	C_4	*Total*
1.	10086,3 fines	6.3	3.8	1.4	5.0	2.9	1.3	0.58	0.20	21.3
2.	10086,3 fines	0.86	1.10	0.25	2.0	0.20	0.19	0.29	0	4.9
3.	Mighei	0	0	0	0.46	0.18	1.34	0.12	0	2.1
4.	Cohenite (Fe_3C)	240	750	0	370	510	690	0	150	2710
5.	Blank	0	0	0	0	0	0	0.24	0.05	0.29

Table 5 Amounts of Carbon (μg/g) Produced as Hydrocarbons During Mild Phosphoric Acid Hydrolysis of Various Lunar Samples

	Experiment		CH_4	C_2H_4	C_2H_2	C_2H_6	C_3H_6	C_3H_8	*Other* C_3	C_4	*Total*
1.	10002,54	(190)*	0.66	0.11	0	0.24	0.034	0.052	0	0.036	1.13
2.	10049	(70)	0.029	0.007	0	0.009	tr**	tr	0	tr	0.045
3.	10057	(16)	0.01	tr	0	tr	tr	tr	0	tr	0.01
4.	10060,22	(134)	0.30	0.10	0	0.27	tr	0.05	0	0.06	0.78
5.	10084	(132)	0.36	0.10	0	0.20	tr	tr	0	tr	0.76
6.	Blank		0	0	0	0	0	0	0	0.39	0.39

*Total carbon content in μg/g presented in parentheses taken from data in reference 2.

**Trace amounts, $< 4 \times 10^{-3}$ μg/g.

Table 6 Concentration and Isotopic Composition of Sulfur in Lunar Fines, Pueblito de Allende and Murray Meteorites, and Troilite from Canyon Diablo Meteorite

Sample	*Sample Weight, g*	*Acid*	$\delta^{34}S$ *(relative to Canyon Diablo meteorite standard)*	*S content, μg/g*
Lunar fines	54.6	1N HCl	+8.6	260
	54.6	6N HCl*	+7.4	412
	1.79	85% H_3PO_4	+5.4	690
	3.01	Aqua regia	+8.2	640
Pueblito de Allende	107.6	1N HCl	+1.1	410
	107.6	6N HCl*	+1.1	5,900
	0.50	2N HCl	+0.9	19,900
	0.48	85% H_3PO_4	+0.7	10,200
Murray	0.28	2N HCl	−0.1	2,600
	0.36	85% H_3PO_4	+0.8	4,600
Canyon Diablo troilite	0.06	2N HCl	+0.5	105,900
	0.04	85% H_3PO_4	+0.2	82,600

*Hydrolysis with 6N HCl followed initial treatment with 1N HCl as described in text.

Table 7 Electron Microprobe Analyses of Glass Spherules Separated from Loose Surface Fines (weight percent)

	Reddish Brown	*Reddish Brown*	*Light Brown*	*Brown*	*Opaque*	*Opaque*	*Dark Brown*
SiO_2	38.4	40.0	43.5	43.0	39.8	37.0	39.4
Al_2O_3	10.0	12.7	12.9	16.7	12.0	5.1	14.5
Cr_2O_3	0.45	0.35	0.32	0.20	0.25	0.65	0.29
TiO_2	6.9	7.2	4.3	4.8	8.3	10.7	7.3
FeO	19.8	16.9	13.6	12.1	17.6	25.0	15.4
MgO	13.9	10.4	14.7	8.9	9.3	14.4	8.6
MnO	0.20	0.16	0.16	0.11	0.17	0.24	0.14
CaO	9.7	11.4	9.9	11.8	12.5	7.3	12.3
Na_2O	0.03	0.07	0.11	0.58	0.56	0.25	0.37
K_2O	<0.02	0.04	<0.02	<0.02	0.08	0.07	0.08
ZrO_2	<0.02	0.04	<0.02	<0.02	0.06	0.05	0.05
P_2O_5	0.03	0.03	0.03	0.03	0.09	0.04	0.07
Total	99.41	99.29	99.52	98.22	100.71	100.80	98.50

Table 8 Electron Microprobe Analyses of Olivines from Apollo 11 Fines (10086,3)

	1	*2*	*3*	*4*	*5*
SiO_2	38.1	37.4	37.3	37.5	36.3
TiO_2	0.08	0.13	0.02	0.11	0.11
Cr_2O_3	0.36	0.21	0.16	0.22	0.27
FeO	21.6	25.3	27.9	28.1	30.8
MnO	0.24	0.33	0.32	0.33	0.45
MgO	39.0	35.6	33.7	33.9	31.4
CaO	0.26	0.31	0.28	0.36	0.30
Total*	99.64	99.28	99.68	100.52	99.63
Number of ions on the basis of 4(0)					
Si	0.993	0.997	1.002	0.999	0.992
Ti	0.007	0.004	0.000	0.005	0.006
Cr	0.002	0.003	0.003	0.002	0.002
Mg	1.516	1.413	1.348	1.347	1.279
Fe	0.471	0.564	0.627	0.626	0.705
Mn	0.005	0.007	0.007	0.008	0.010
Ca	0.007	0.009	0.008	0.010	0.009
X	0.993	0.997	1.002	0.999	0.992
Y	2.008	2.000	1.983	1.998	2.011
Z	3.001	2.997	2.985	2.997	3.003
Fo	76.3	71.5	68.3	68.3	64.5
Fa	23.7	28.5	31.7	31.7	35.5

*NiO <0.01 percent in all cases

Table 9 Electron Microprobe Analyses of Pyroxenes from Apollo 11 Fines (10086,3)

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*
SiO_2	50.0	51.1	49.3	49.4	50.6	49.2	50.7	51.0	51.9	49.8	51.4	50.4	50.9	50.1	49.4	48.6	49.0
Al_2O_3	4.0	2.83	4.06	3.6	2.69	4.0	2.52	1.49	1.80	2.99	1.26	2.05	1.30	1.53	1.49	1.40	1.20
Cr_2O_3	0.74	0.66	0.76	0.62	0.63	0.65	0.50	0.51	0.36	0.56	0.23	0.41	0.28	0.23	0.22	0.16	0.22
TiO_2	3.3	2.27	3.5	3.3	2.31	3.5	2.23	2.15	1.82	2.53	1.30	1.77	1.31	5.0	1.58	1.35	1.31
FeO	8.3	8.8	9.5	10.3	10.6	11.0	11.2	11.5	11.7	11.8	16.3	17.5	18.0	19.0	23.3	26.9	27.8
MgO	14.4	15.9	14.6	15.2	16.6	14.0	15.6	16.2	15.7	14.8	13.9	14.4	13.9	11.1	10.8	6.9	10.1
MnO	0.19	0.20	0.24	0.24	0.26	0.33	0.26	0.24	0.29	0.19	0.42	0.40	0.41	0.20	0.55	0.70	0.55
CaO	19.4	18.3	18.0	17.7	16.0	17.2	17.3	17.2	16.5	16.2	14.4	12.5	13.6	14.2	12.2	13.5	9.2
Na_2O	0.09	0.08	0.06	0.10	0.04	0.08	0.08	0.03	0.06	0.09	0.05	0.03	0.05	0.04	0.03	0.03	0.05
	100.42	100.14	100.02	100.46	99.73	99.96	100.39	100.32	100.13	98.96	99.26	99.46	100.20	101.40	99.57	99.54	99.43
Number of ions on the basis of 6(0)																	
Si	1.847	1.889	1.836	1.839	1.885	1.839	1.887	1.902	1.931	1.880	1.960	1.922	1.943	1.896	1.935	1.947	1.948
Al	0.153	0.111	0.165	0.158	0.115	0.161	0.110	0.066	0.069	0.120	0.040	0.078	0.058	0.068	0.065	0.053	0.052
Al	0.022	0.111	0.014	0.000	0.003	0.017	0.000	0.000	0.010	0.013	0.017	0.014	0.001	0.000	0.003	0.014	0.004
Cr	0.022	0.019	0.022	0.018	0.019	0.019	0.015	0.015	0.011	0.017	0.007	0.012	0.009	0.007	0.007	0.005	0.007
Ti	0.092	0.063	0.098	0.091	0.065	0.100	0.062	0.060	0.051	0.072	0.037	0.051	0.038	0.143	0.047	0.041	0.039
Fe	0.256	0.273	0.300	0.320	0.329	0.344	0.349	0.359	0.364	0.373	0.518	0.557	0.576	0.600	0.761	0.900	0.924
Mg	0.795	0.875	0.810	0.841	0.920	0.782	0.866	0.901	0.869	0.835	0.788	0.817	0.792	0.626	0.632	0.414	0.596
Mn	0.006	0.006	0.008	0.008	0.008	0.010	0.008	0.008	0.009	0.006	0.014	0.013	0.013	0.006	0.018	0.024	0.019
Ca	0.767	0.724	0.716	0.706	0.638	0.688	0.689	0.686	0.658	0.655	0.588	0.511	0.556	0.575	0.512	0.578	0.390
Na	0.006	0.006	0.004	0.007	0.003	0.006	0.006	0.002	0.004	0.007	0.004	0.002	0.004	0.003	0.002	0.002	0.004
Z	2.000	2.000	2.000	1.997	2.000	2.000	1.997	1.968	2.000	2.000	2.000	2.000	2.000	1.964	2.000	2.000	2.000
WXY	1.966	1.977	1.972	1.991	1.985	1.966	1.995	2.031	1.976	1.978	1.973	1.977	1.989	1.960	1.982	2.018	1.983
Σ	3.966	3.977	3.972	3.988	3.985	3.966	3.992	3.999	3.976	3.978	3.973	3.977	3.989	3.944	3.982	4.018	3.983
Molecular Percent																	
En	43.7	46.7	44.4	45.0	48.8	43.1	45.4	46.3	46.0	44.8	41.6	43.3	41.2	34.7	33.1	21.9	31.2
Fs	14.1	14.6	16.4	17.1	17.4	18.9	18.3	18.4	19.2	19.5	27.3	29.5	29.9	33.3	39.9	47.6	48.4
Wo	42.2	38.7	39.2	37.9	33.8	38.0	36.3	35.3	34.8	35.2	31.1	27.2	28.9	32.0	27.0	30.5	20.4

Table 10 Electron Microprobe Analyses of Plagioclase from Apollo 11 Fines (10086,3)

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*	*20*
SiO_2	44.2	44.7	44.9	44.9	45.0	45.0	45.1	45.3	45.4	45.4	45.5	45.8	45.9	46.1	46.2	46.6	47.1	47.9	49.2	49.2
Al_2O_3	35.6	34.4	35.4	35.0	35.2	34.6	35.3	34.6	33.3	34.8	33.6	33.5	33.8	34.1	34.0	33.4	33.2	32.9	31.5	32.4
FeO	0.19	0.23	0.20	0.10	0.13	0.43	0.14	0.15	0.24	0.45	0.23	0.34	0.06	0.14	0.30	0.35	0.24	0.13	0.68	0.54
CaO	19.7	19.4	19.3	19.3	19.3	19.3	19.6	19.4	18.6	19.3	18.7	18.6	19.0	18.8	18.6	18.0	17.6	17.6	17.0	17.1
Na_2O	0.36	0.45	0.60	0.53	0.54	0.40	0.38	0.42	0.85	0.45	0.75	0.84	0.73	0.77	0.85	1.03	1.20	1.38	1.36	1.49
K_2O	<0.01	0.02	0.02	0.03	<0.01	<0.01	<0.01	0.05	0.03	0.08	0.02	0.02	0.01	0.08	<0.01	<0.01	0.01	0.05	0.09	0.06
	100.05	99.20	100.42	99.86	100.17	99.73	100.52	99.92	98.42	100.48	98.80	99.10	99.50	99.99	99.95	99.38	99.35	99.96	99.83	100.79
Number of ions on the basis of 32(0)																				
Si	8.178	8.334	8.266	8.307	8.298	8.343	8.290	8.374	8.514	8.356	8.496	8.528	8.506	8.501	8.521	8.628	8.706	8.794	9.036	8.949
Al	7.763	7.559	7.681	7.631	7.650	7.561	7.647	7.538	7.360	7.549	7.395	7.351	7.382	7.411	7.390	7.289	7.233	7.119	6.818	6.946
Fe	0.029	0.036	0.031	0.016	0.020	0.067	0.022	0.023	0.038	0.069	9.036	0.053	0.009	0.022	0.046	0.054	0.037	0.020	0.104	0.082
Na	0.129	0.163	0.214	0.190	0.193	0.144	0.135	0.151	0.309	0.161	0.271	0.303	0.262	0.275	0.304	0.370	0.430	0.491	0.484	0.526
Ca	3.905	3.875	3.807	3.826	3.813	3.834	3.860	3.842	3.737	3.806	3.741	3.711	3.773	3.714	3.675	3.571	3.486	3.462	3.345	3.332
K	-	0.005	0.005	0.007	-	-	-	0.012	0.007	0.019	0.005	0.005	0.002	0.019	-	-	0.002	0.012	0.021	0.014
Z	15.941	15.893	15.947	15.937	15.948	15.904	15.937	15.912	15.874	15.905	15.891	15.879	15.888	15.912	15.911	15.917	15.939	15.913	15.854	15.895
X	4.053	4.079	4.057	4.039	4.026	4.045	4.017	4.028	4.091	4.055	4.053	4.072	4.046	4.030	4.025	3.995	3.955	3.985	3.954	3.954
Σ	19.994	19.972	20.004	19.976	19.974	19.949	19.954	19.940	19.965	19.960	19.944	19.951	19.934	19.942	19.936	19.912	19.894	19.898	19.808	19.849
Ab	3.2	4.0	5.3	4.7	4.8	3.4	3.0	3.8	7.6	4.0	6.7	7.5	6.5	6.9	7.6	8.4	11.0	12.4	12.6	13.6
An	96.8	95.8	94.6	95.1	95.2	96.6	97.0	95.9	92.2	95.5	93.1	92.3	93.5	92.7	92.4	90.6	89.0	87.3	86.9	86.1
Or	0	0.2	0.1	0.2	0	0	0	0.3	0.2	0.5	0.2	0.2	<0.1	0.4	0	0	<0.1	0.3	0.5	0.3

Table 11 Electron Microprobe Analyses of Green Glass from Apollo 11 Fines (10086,3)

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
SiO_2	44.0	44.0	44.6	44.7	44.9	45.0	45.0	45.2	49.4	50.5
Al_2O_3	26.6	21.0	25.6	25.8	25.3	26.5	26.0	26.4	21.9	16.5
Cr_2O_3	0.10	0.26	0.11	0.09	0.11	0.11	0.11	0.10	0.06	0.15
TiO_2	0.31	0.50	0.41	0.37	0.44	0.38	0.38	0.36	0.14	2.2
FeO	5.8	9.5	6.1	5.8	6.0	6.0	5.8	6.2	4.1	10.7
MgO	7.7	9.7	7.6	7.7	7.4	7.9	8.0	8.0	9.4	7.7
MnO	0.05	0.11	0.13	0.12	0.11	0.11	0.06	0.05	0.06	0.19
CaO	14.7	12.7	14.7	14.9	14.5	14.8	14.4	14.6	15.2	10.5
Na_2O	0.18	0.17	0.15	0.07	0.15	0.07	0.03	0.11	0.48	0.41
K_2O	0.02	0.05	0.02	0.03	0.04	0.02	0.01	0.03	<0.01	0.34
ZrO_2	0.02	0.04	0.03	0.02	0.04	<0.01	0.01	0.02	<0.01	0.27
P_2O_5	0.02	0.04	0.04	0.06	0.03	0.02	0.02	0.04	0.02	0.23
	99.50	98.07	99.49	99.66	99.52	100.91	99.82	101.11	100.76	99.69

Table 12 Electron Microprobe Analyses of Amber Glass from Apollo 11 Fines (10086,3)

	1	*2*	*3*	*4*	*5*	*6*
SiO_2	40.4	41.3	41.5	41.7	42.2	47.6
Al_2O_3	12.7	11.2	12.8	12.7	16.7	15.3
Cr_2O_3	0.40	0.31	0.39	0.36	0.27	0.17
TiO_2	8.2	9.3	7.5	7.2	5.8	2.35
FeO	18.2	17.1	15.3	14.9	12.4	11.7
MgO	7.0	7.8	9.4	9.3	8.5	10.4
MnO	0.30	0.24	0.23	0.23	0.19	0.14
CaO	10.7	11.1	10.7	10.8	11.8	9.9
Na_2O	0.42	0.38	0.39	0.42	0.35	0.09
	98.21	98.73	97.55	97.61	98.21	97.55

Table 13 Summary of Fluorescence Spectral Data

	Excitation, nm			*Emission, nm*	
6N HCl	386	517	550	600	630
Acetic	390	523	562	(595)	625
Ether	418	455	512	625	
MSA	410			660	

Table 14 Methyl Esters of Fatty Acids (μg/g)

	Methanol from Benzene-Methanol		*BF_3-Methanol Extract*	
Compound	*ARC-1*	*BLANK*	*ARC-1*	*BLANK*
C_{14}	+	+	?	?
C_{15}	+	–	+	–
$C_{16:0}$	$\sim 8 \times 10^{-3}$	$\sim 8 \times 10^{-3}$	$\sim 10^{-3}$	$\sim 10^{-3}$
$C_{16:1}$	$\sim 2 \times 10^{-3}$	$\sim 1 \times 10^{-3}$	$\sim 10^{-3}$	?
C_{17}	?	–	+	–
$C_{18:0}$	$\sim 6 \times 10^{-3}$	$\sim 6 \times 10^{-7}$	$\sim 10^{-3}$	$\sim 10^{-3}$
$C_{18:0}$	$\sim 4 \times 10^{-3}$	$\sim 3 \times 10^{-3}$	$\sim 10^{-3}$	+
C_{19}	?	–	+	–
C_{20}	?	–	+	–
Unknowns	+	–	–	–

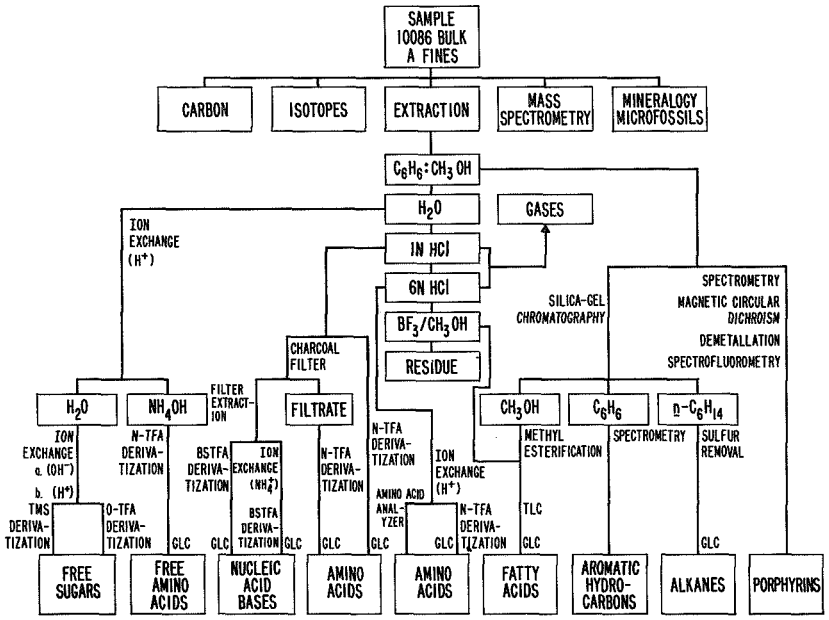


Figure 1 Scheme of analysis.

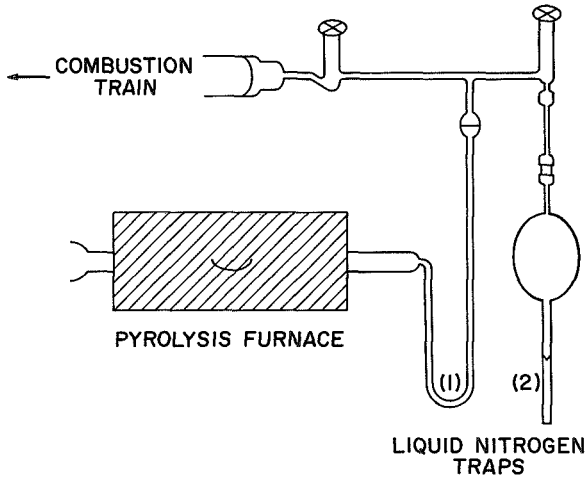


Figure 2 Pyrolysis apparatus.

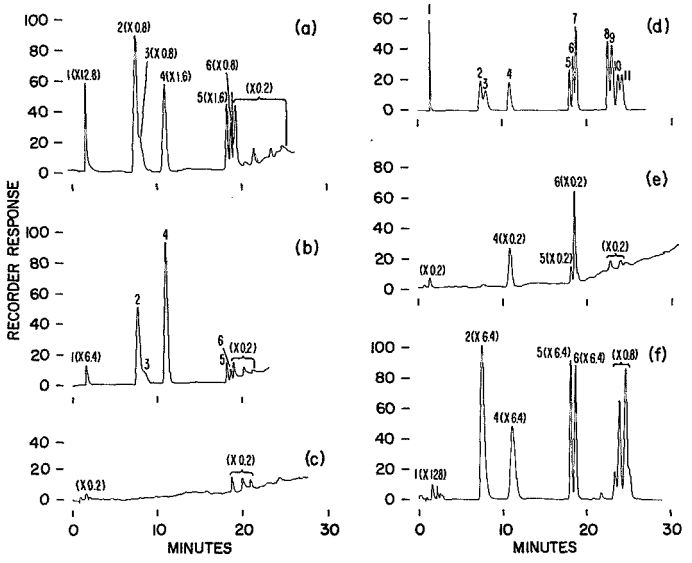


Figure 3 Gas chromatograms of hydrocarbons obtained from: (a) and (b) HCl treatment of 10086,3 Bulk A fines; (c) control blank; (d) standard mixture containing about 20 μl each of (1) methane, (2) ethene, (3) acetylene, (4) ethane, (5) propene, (6) propane, (7) allene, (8) isobutane, (9) butene-1, (10) butane, (11) cis-2-butene (attenuation X160 throughout run); (e) and (f) HCl treatment of Mighei meteorite and cohenite (Fe_3C), respectively. A 6 in. by 0.125 -in. stainless steel column packed with 100 to 120-mesh Poropak Q was used on a Varian Model 1520 B gas chromatograph equipped with flame detector. Flow rate was 20 ml/min. Oven temperature initially held at 35° C for 10 min, then programmed at 10°/min to 140° C where it was held. Unless otherwise indicated, peak attenuations were X0.4. Each injection represented 7 percent of the total sample.

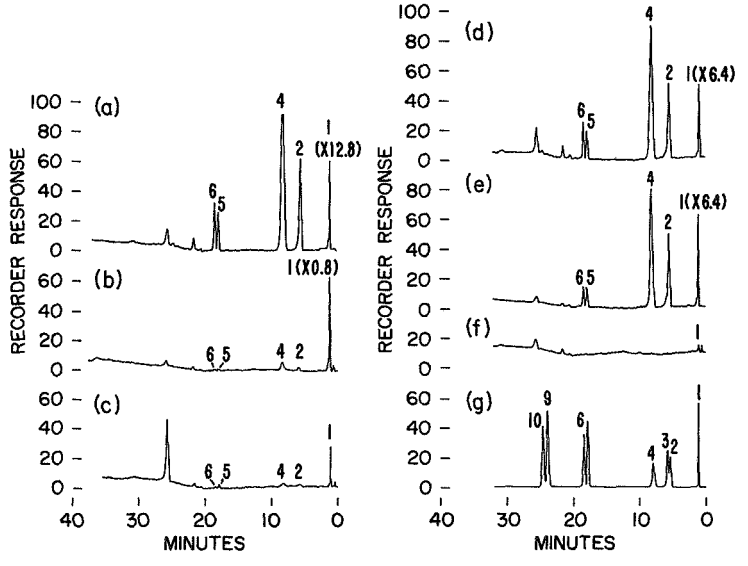


Figure 4 Gas chromatograms of hydrocarbons obtained from H_3PO_4 treatment of lunar samples. Conditions were same as on figure 3 except that helium flow was 30 ml/min. (a) 10002,54; (b) 10049; (c) 10057; (d) 10060,22; (e) 10084; (f) control blank; (g) standard mixture containing 2 μl of each gas (identified in figure 3), attenuation X64.

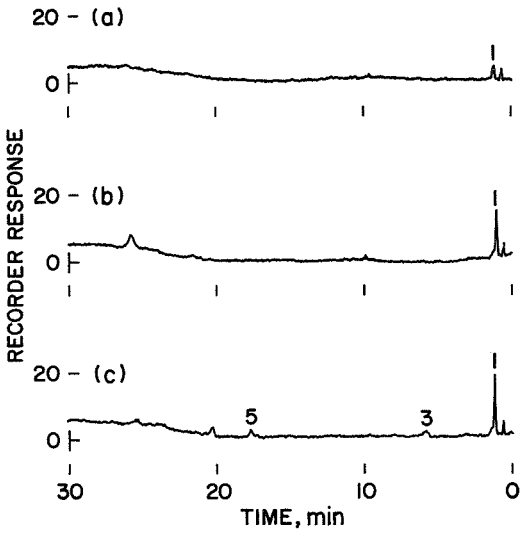


Figure 5 Gas chromatograms of hydrocarbons produced by pyrolysis of 10086,3 lunar fines. Conditions were as on figure 4 except that 0.4 percent of each sample was injected. (a) 150°–250° C; (b) 250°–500° C; (c) 500°–750° C.

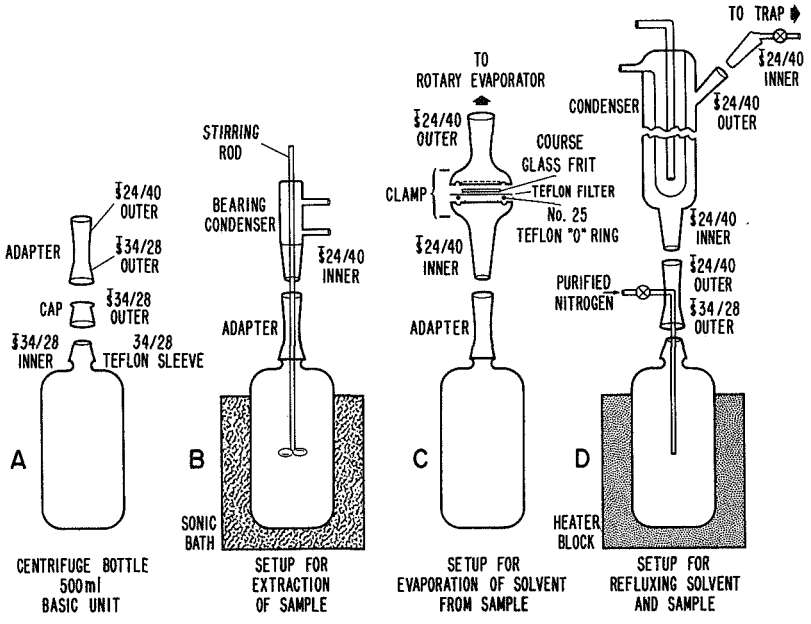


Figure 6 Glassware used in sequential extraction of lunar sample.

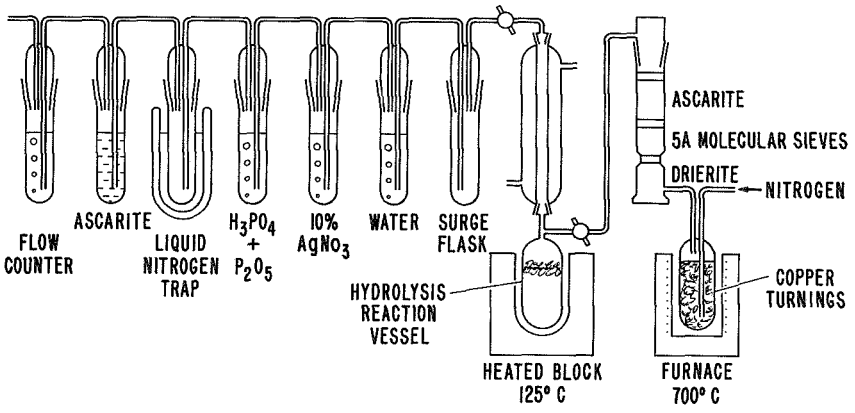


Figure 7 System for trapping gases evolved during hydrolysis.

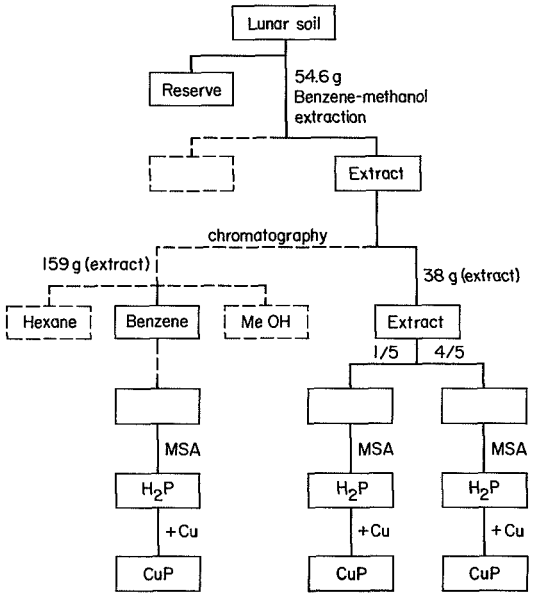


Figure 8 Flow sheet detail for porphyrin analysis.

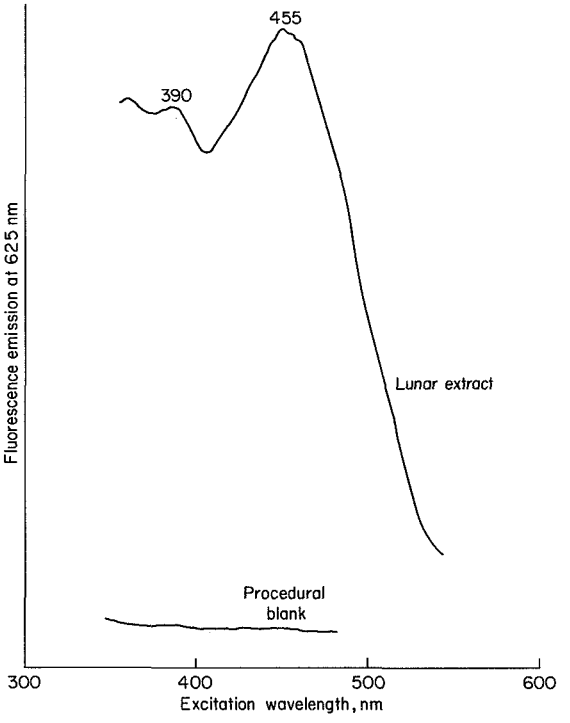


Figure 9 Fluorescence of concentrated lunar extract with procedural blank.

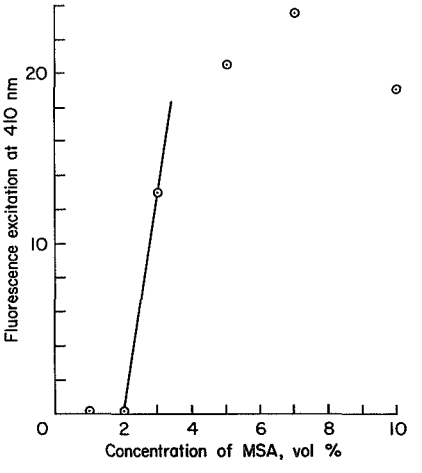


Figure 10 Methanesulfonic acid demetallation analysis showing onset of apparent demetallation at 2 percent MSA.

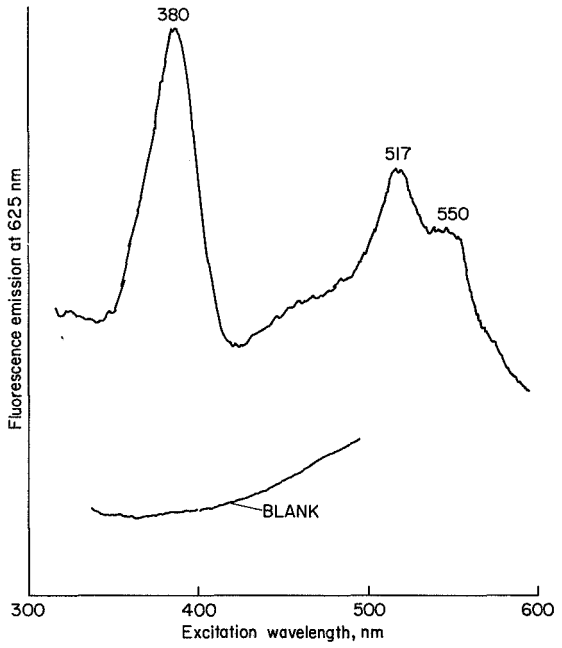


Figure 11 Spectrum of lunar porphyrin-like material in hydrochloric acid.

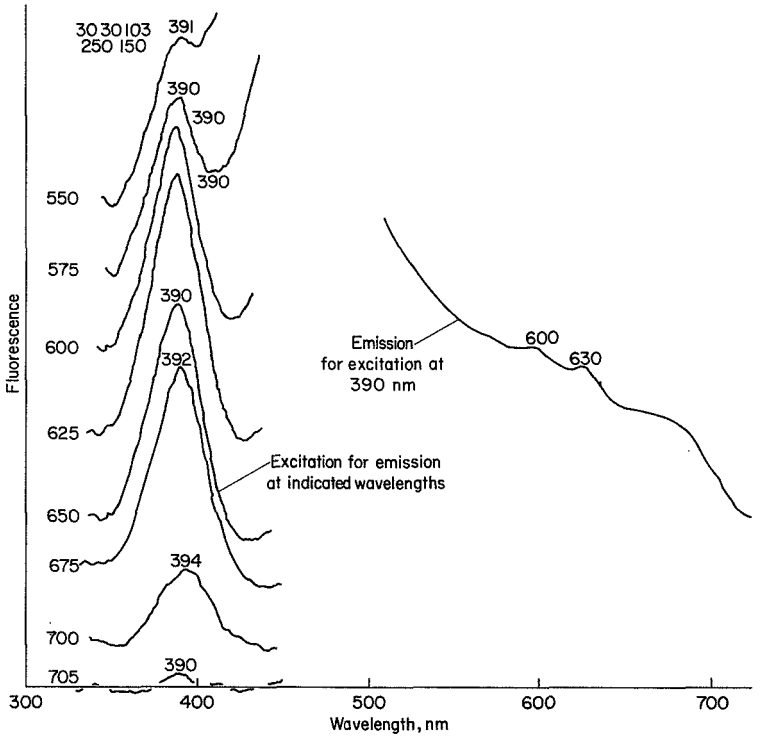


Figure 12 Excitation and emission spectra of pigments in lunar sample.

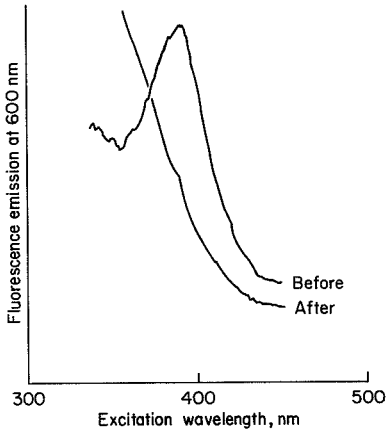


Figure 13 Fluorescence excitation spectra showing the nonfluorescing properties of the copper complex of the lunar pigment.

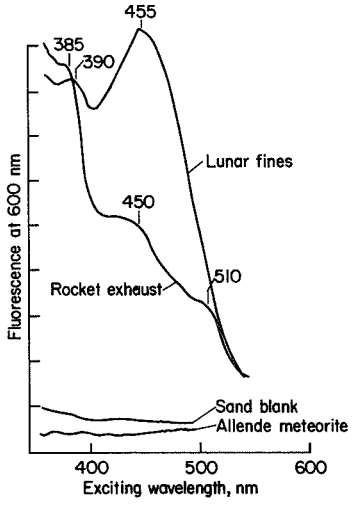


Figure 14 Fluorescence excitation spectra for extracts of lunar fines; dunite exposed to exhaust of a rocket engine fired at NASA White Sands Test Facility; crushed Pueblito de Allende carbonaceous chondrite; and Ottawa sand ignited at 1000° C for 48 hr. Instrument operating parameters were set for highest sensitivity in all cases except for the rocket exhaust in which fluorescence was suppressed by a factor of 20.

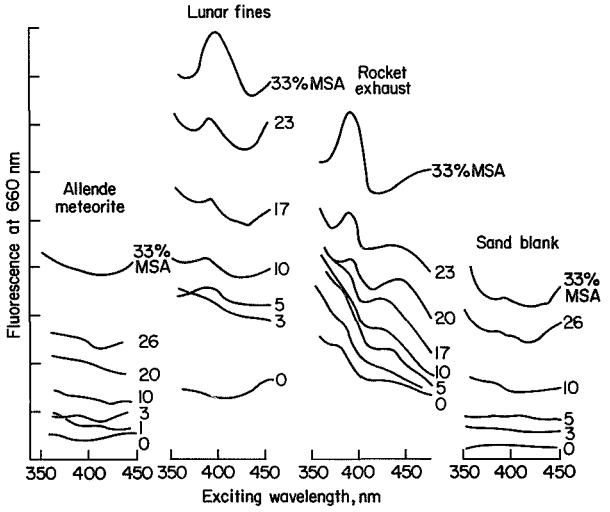


Figure 15 Demetallation analysis of extracts showing emergence of excitation peaks in the region of the Soret band of porphyrins with increasing content of MSA. Instrument operating parameters the same in all cases; aliquots taken for analyses of lunar fines and rocket exhaust were, respectively, 75 percent and 11 percent of the total extracts.

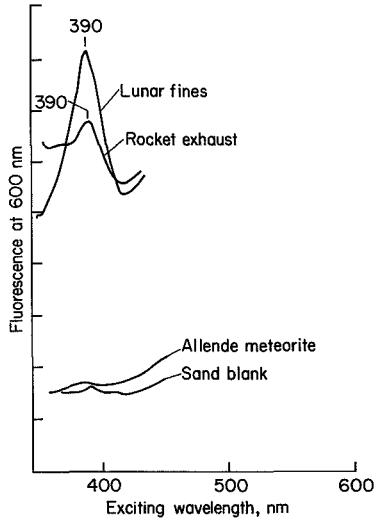


Figure 16 Fluorescence excitation spectra in Soret region for pigments recovered from MSA demetallation analyses. Operating parameters for spectrofluorometer same in all cases; solvent 6N HCl.

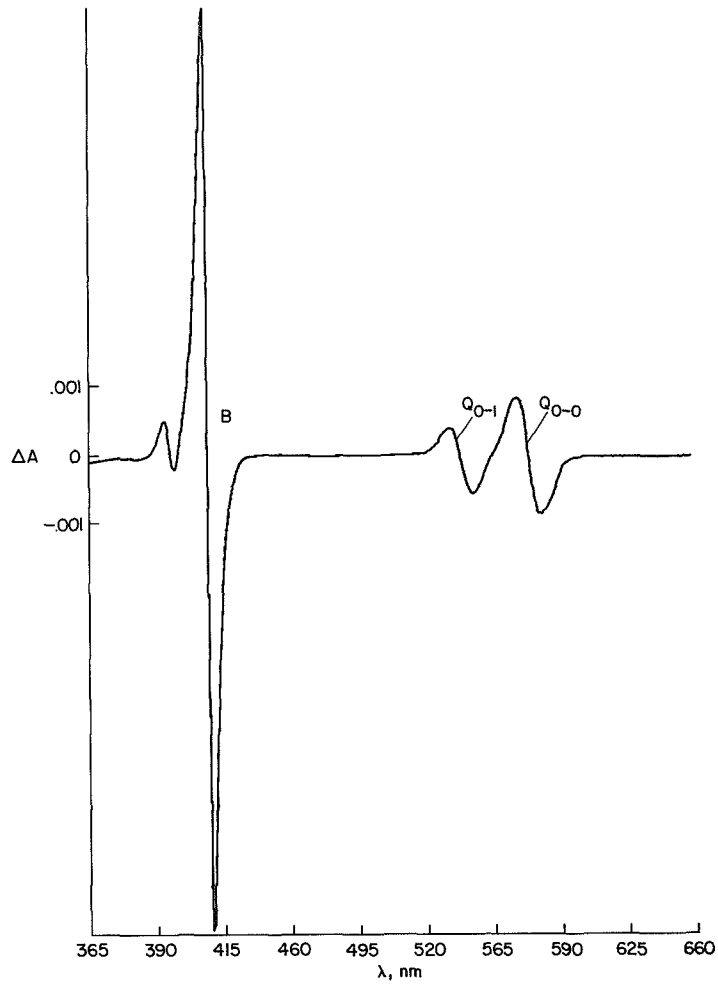
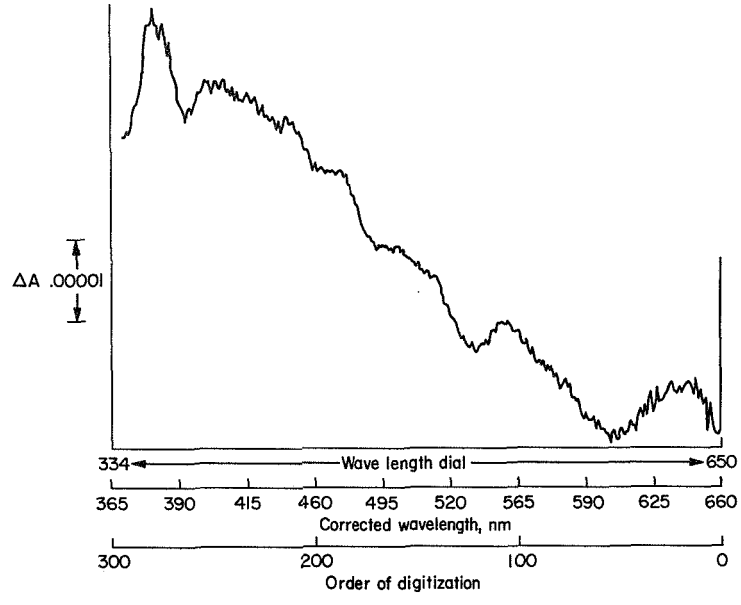
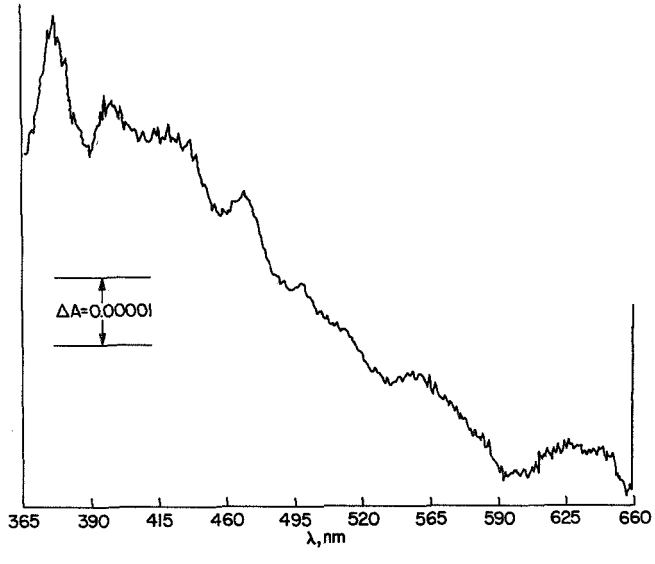


Figure 17 Magnetic circular dichroism spectrum of Mg(II) deuteroporphyrin IX dimethyl ester in 95 percent ethanol recorded under the conditions used for measurement of the lunar sample extract; c = 2.24 μg/ml.

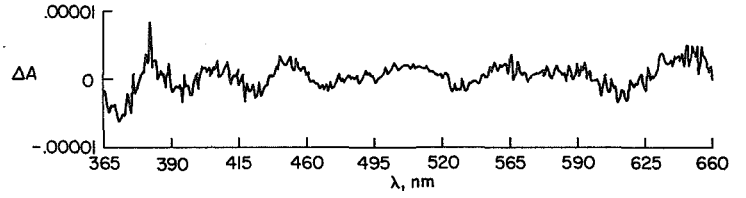


(a) Integrated signal divided by time.

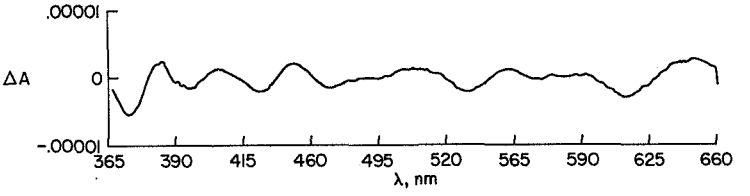


(b) Methanol baseline for lunar sample from integrated signal divided by time.

Figure 18 Magnetic circular dichroism curve of the lunar extract.

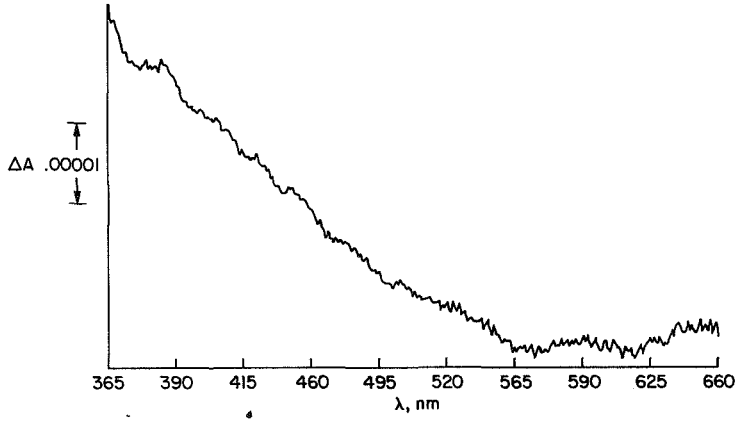


(c) Curve corrected for solvent baseline.



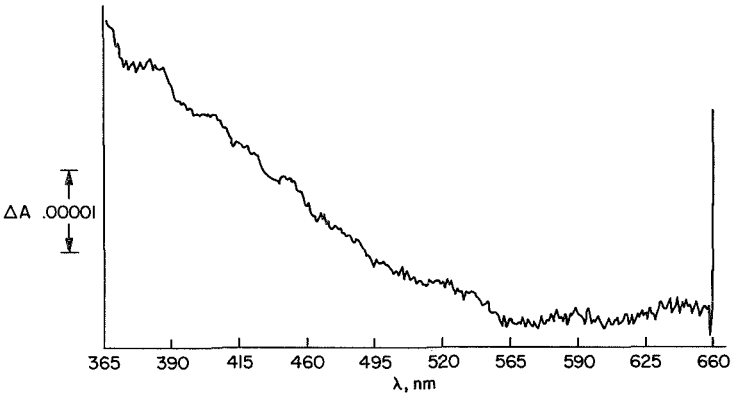
(d) Smoothed (21 point) curve corrected for solvent baseline.

Figure 18 Concluded.

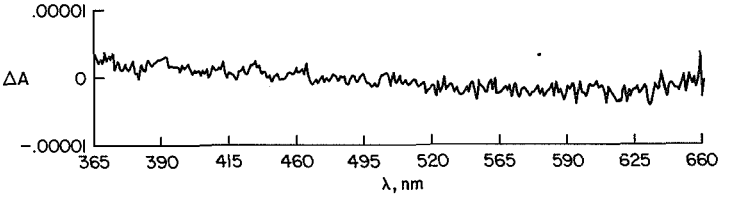


(a) Integrated signal divided by time.

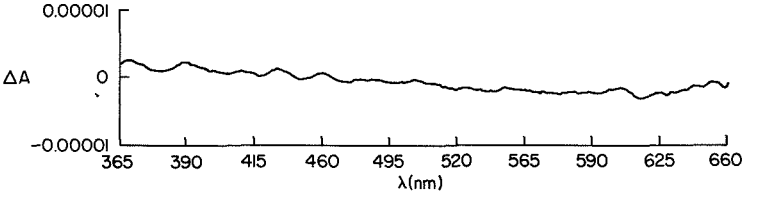
Figure 19 Magnetic circular dichroism curve of the sand blank sample.



(b) Corresponding solvent baseline.



(c) Curve corrected for solvent baseline.



(d) Smoothed (21 point) curve corrected for solvent baseline.

Figure 19 Concluded.

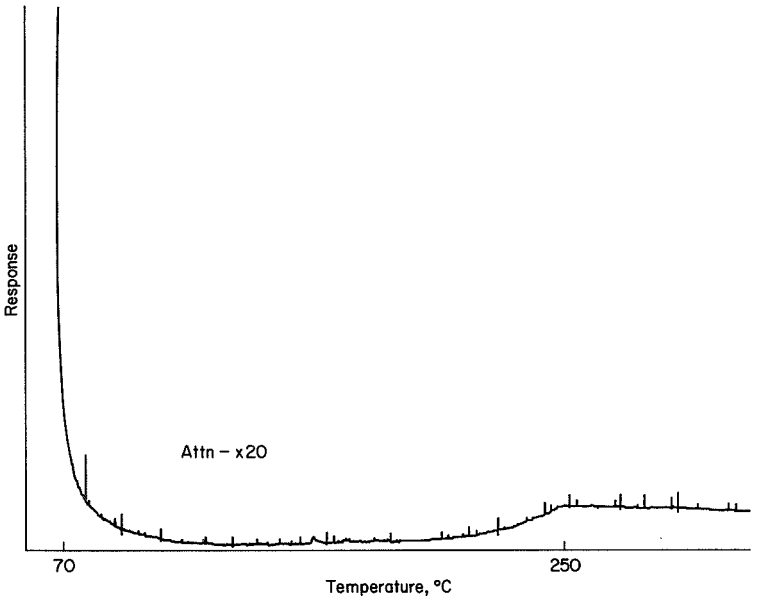


Figure 20 Gas chromatogram of hexane blank showing background for figures 21 and 22. Temperature programmed at 2°/min.

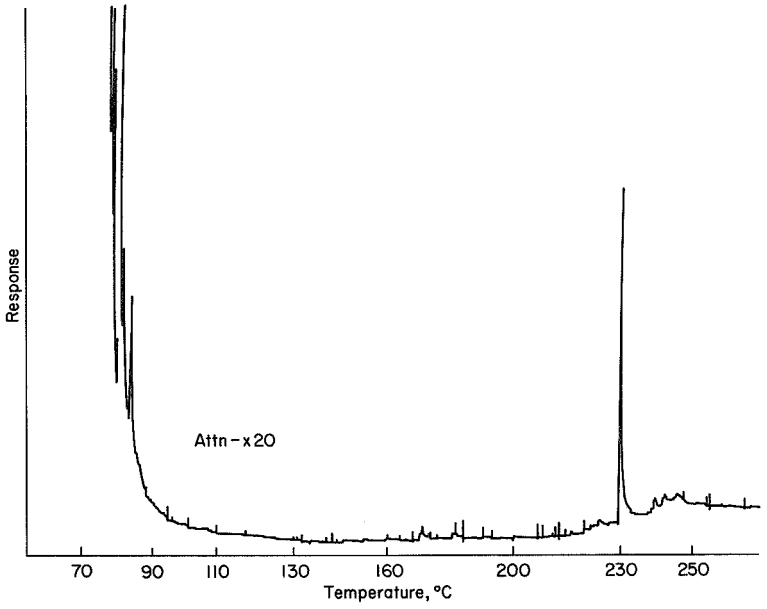


Figure 21 Gas chromatogram of alkane fraction of sand run as a control to determine the level of possible contamination. Temperature programmed at 2°/min.

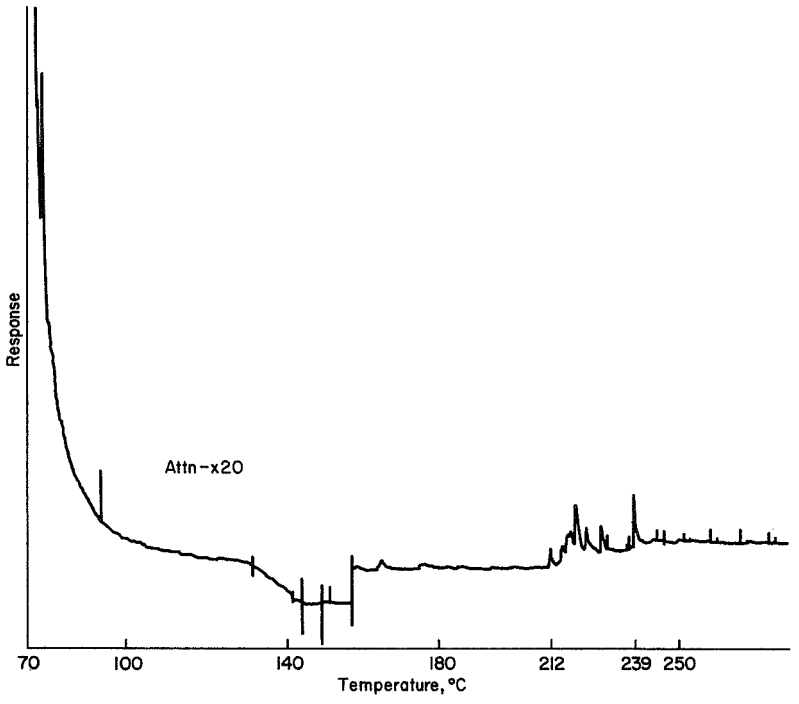


Figure 22 Gas chromatogram of 10 percent of alkane fraction of lunar sample. Temperature programmed at 2°/min.

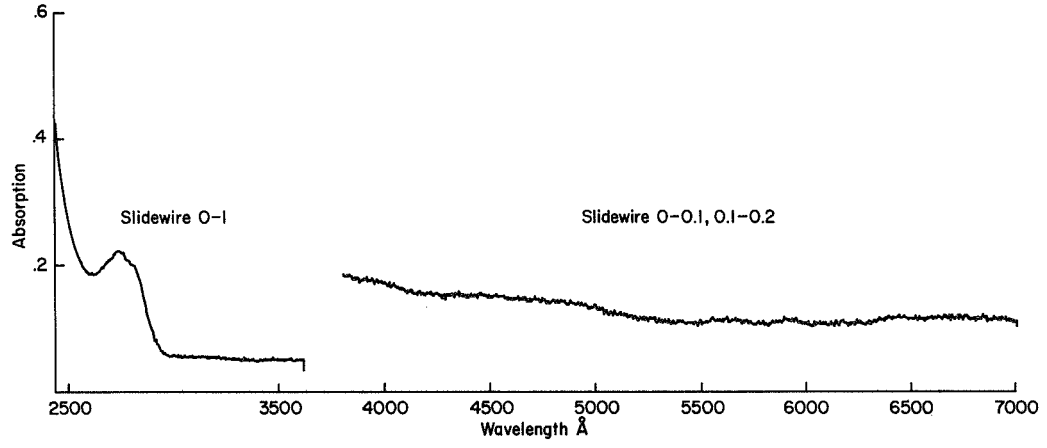


Figure 23 Ultraviolet-visible spectra from benzene eluate of sand blank.

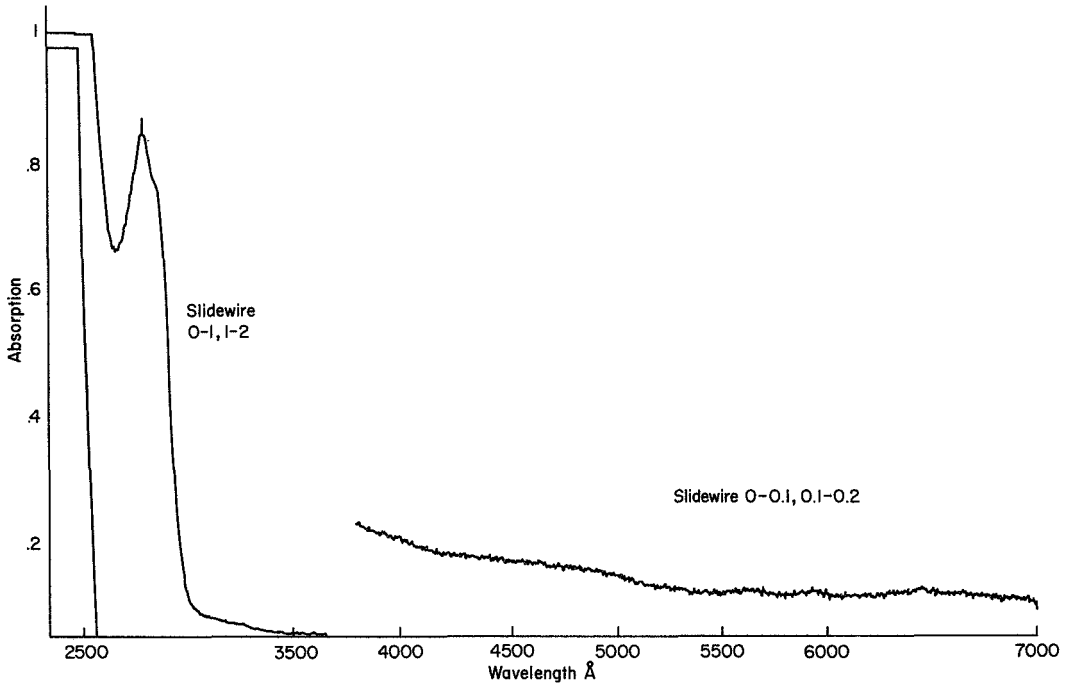


Figure 24 Ultraviolet-visible spectra from benzene eluate of lunar sample.

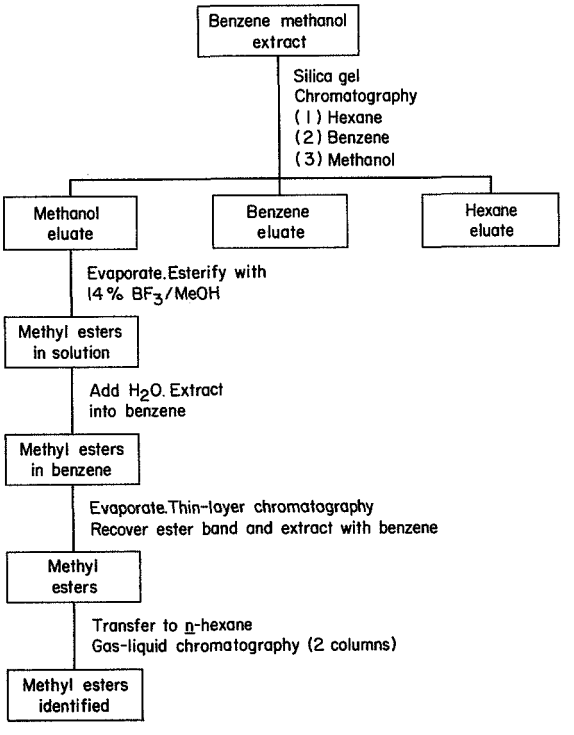


Figure 25 Scheme for the preparation of methyl esters of fatty acids from methanol eluate from silica gel chromatography of benzene-methanol extract.

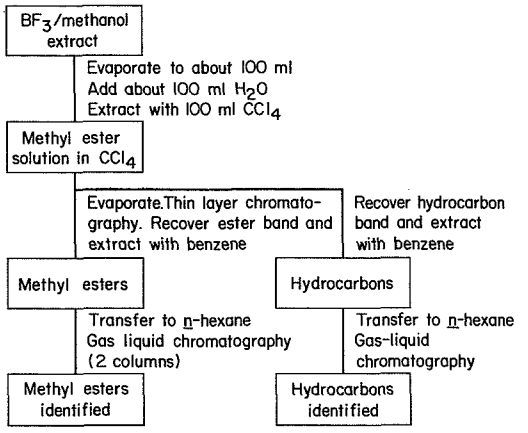


Figure 26 Scheme for the determination of methyl esters of fatty acids from BF_3-methanol extract.

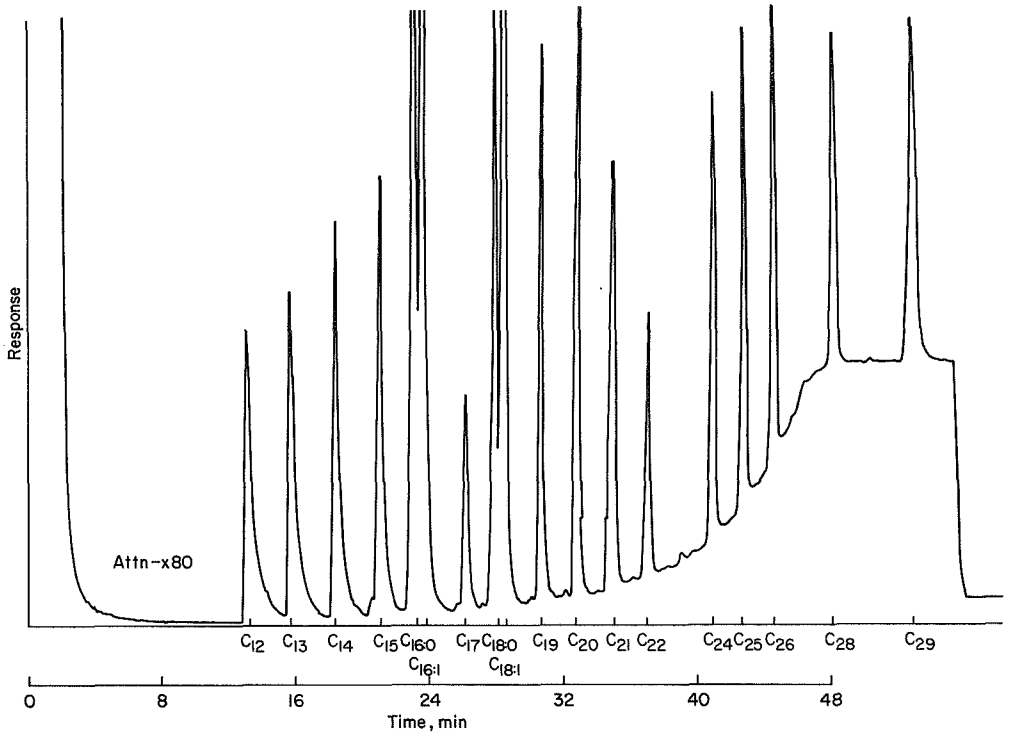


Figure 27 Gas chromatogram of standard of methyl esters of fatty acids obtained on column containing 3 percent SE-30 on gas Chromasorb Z. Temperature programmed at 4°/min from 118° to 280° C.

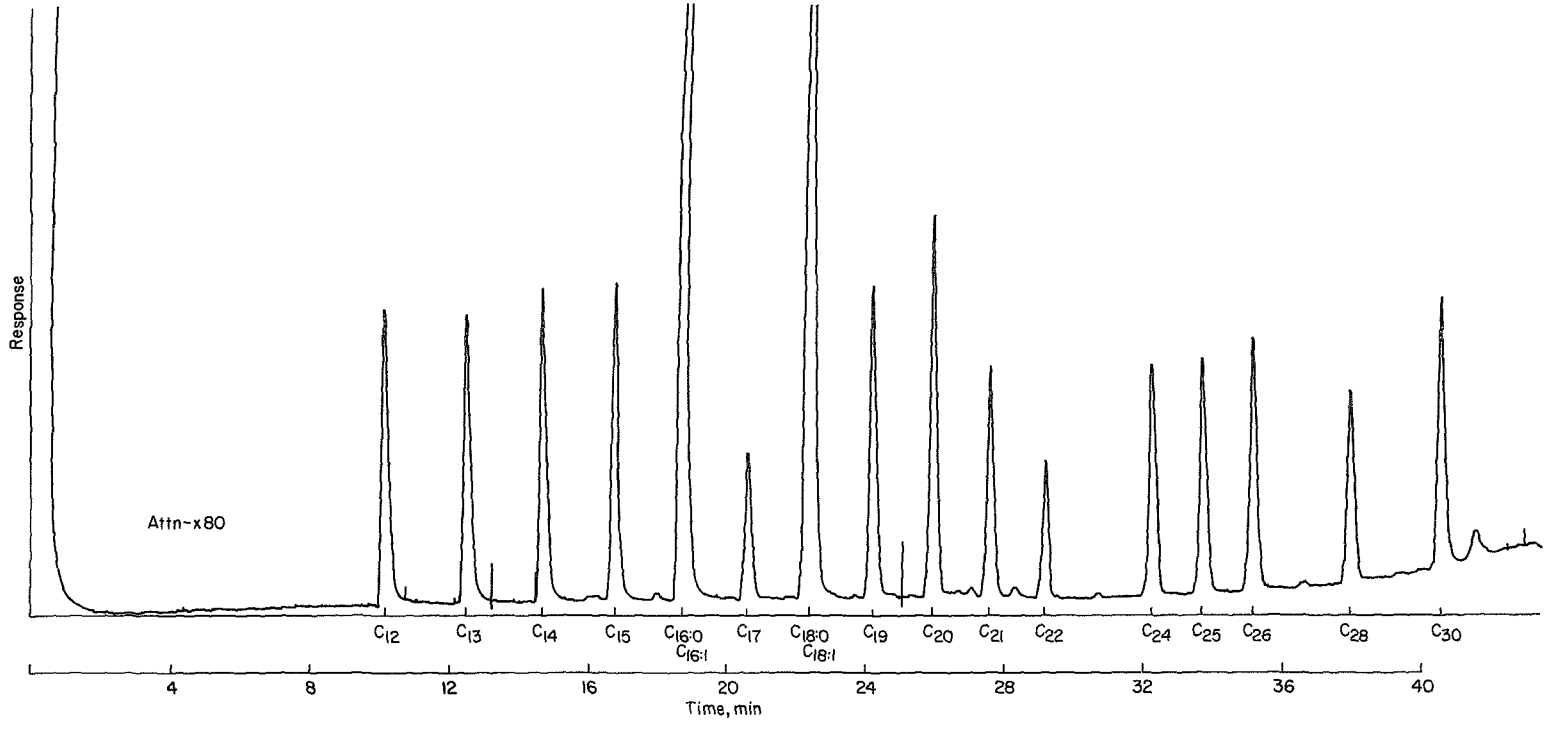
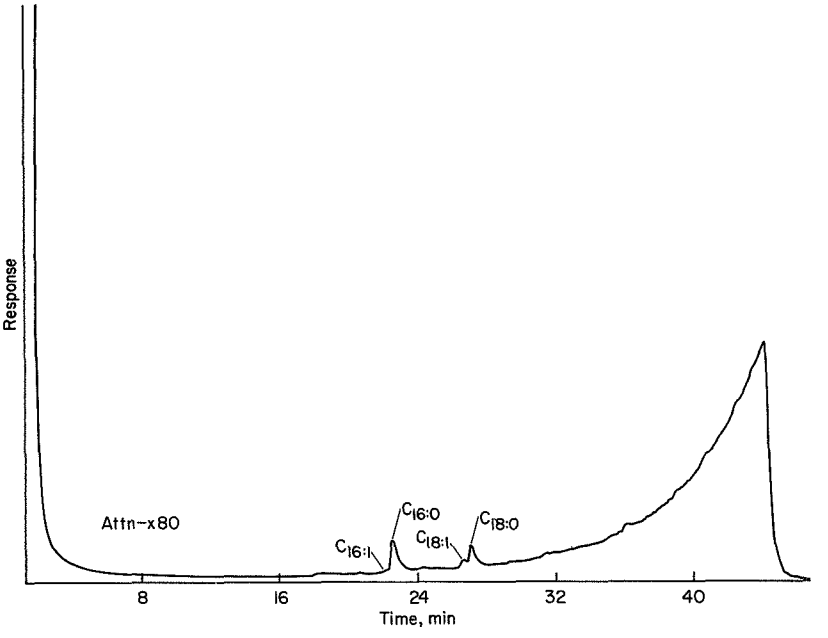
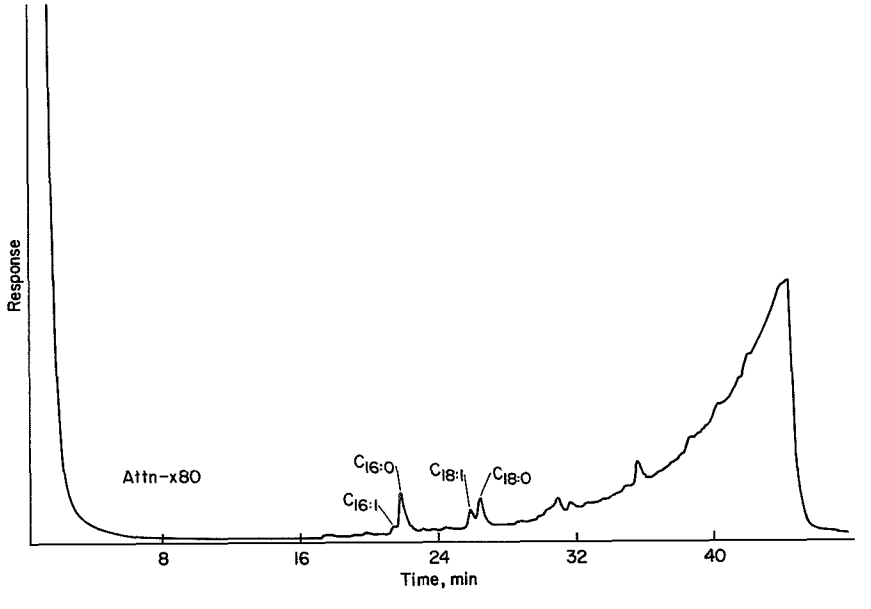


Figure 28 Gas chromatogram of standard of methyl esters of fatty acids obtained on a column containing 3 percent OV-17 on gas Chromasorb Q. Temperature programmed at 5°/min from 100° to 310° C.

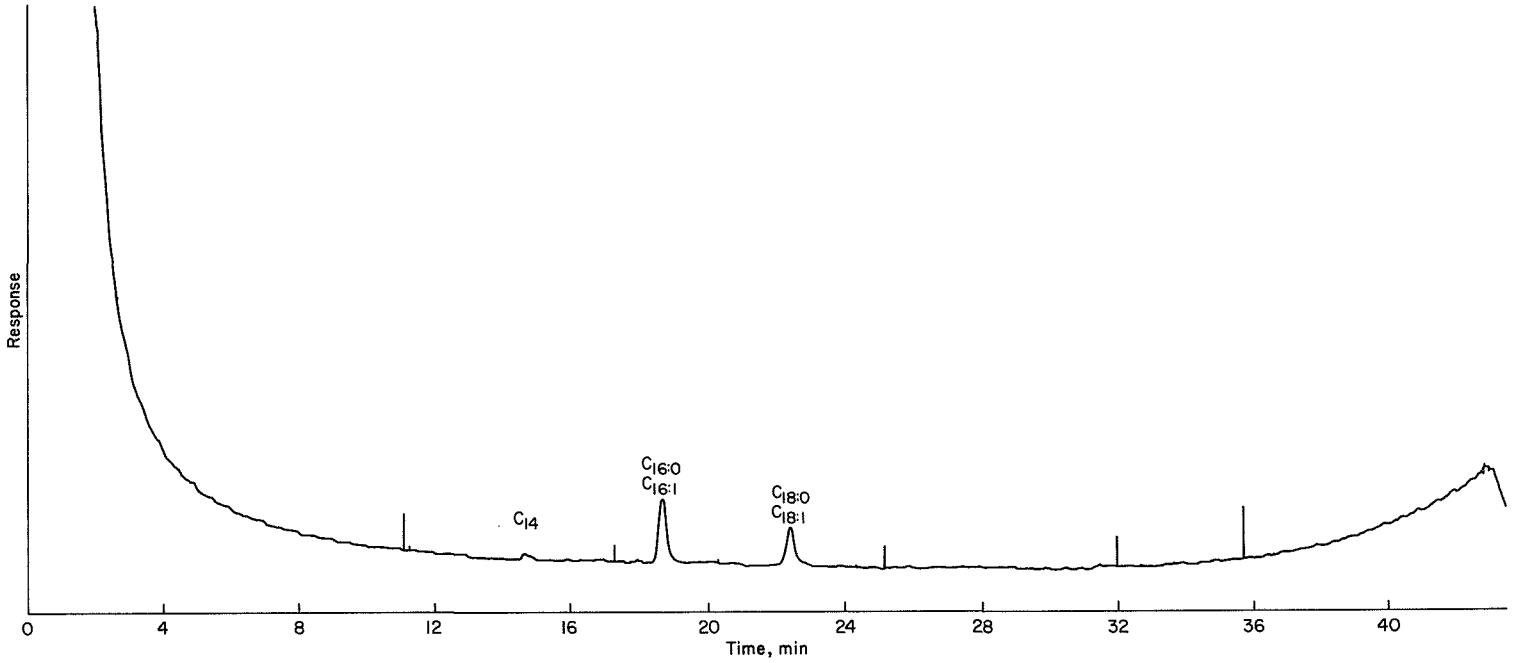


(a) Sand blank. Chromatographic conditions as on figure 27.



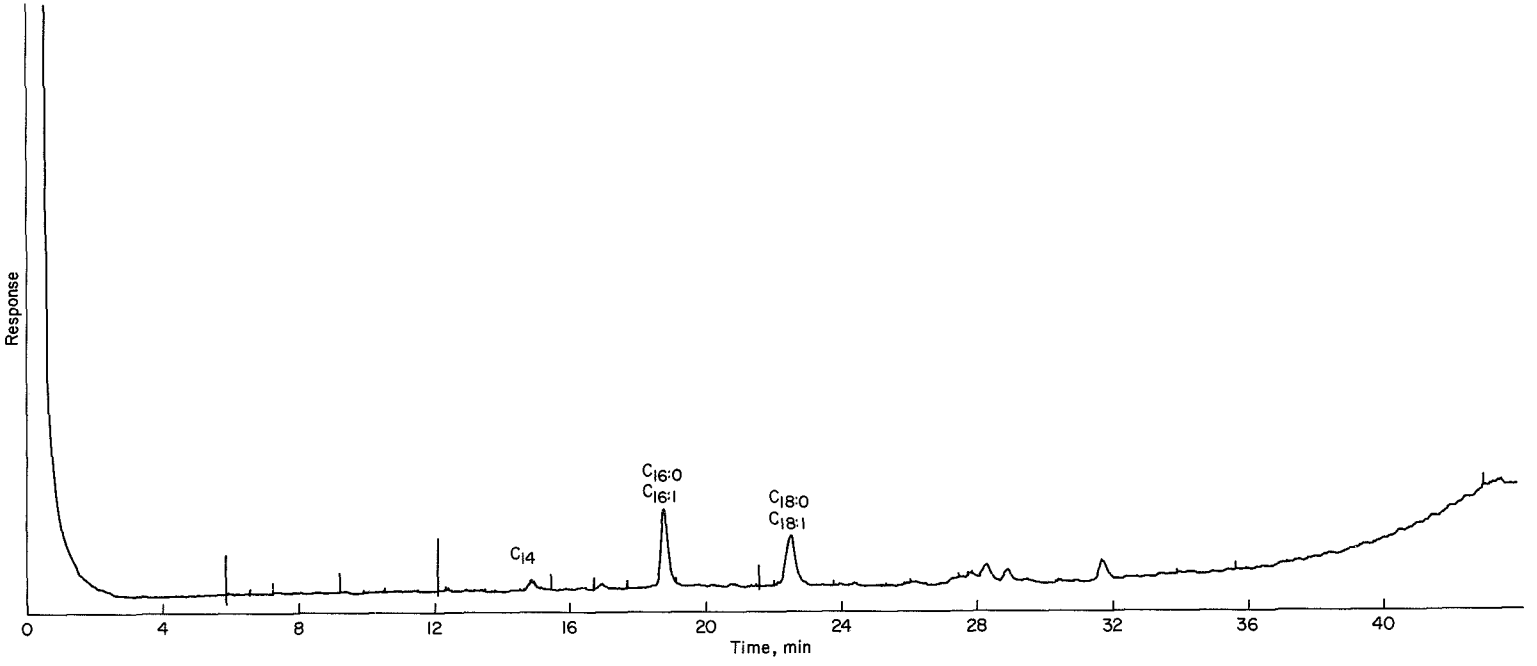
(b) Lunar sample. Chromatographic conditions as on figure 27.

Figure 29 Gas chromatograms of methyl esters of fatty acids in 10 percent benzene-methanol extract.



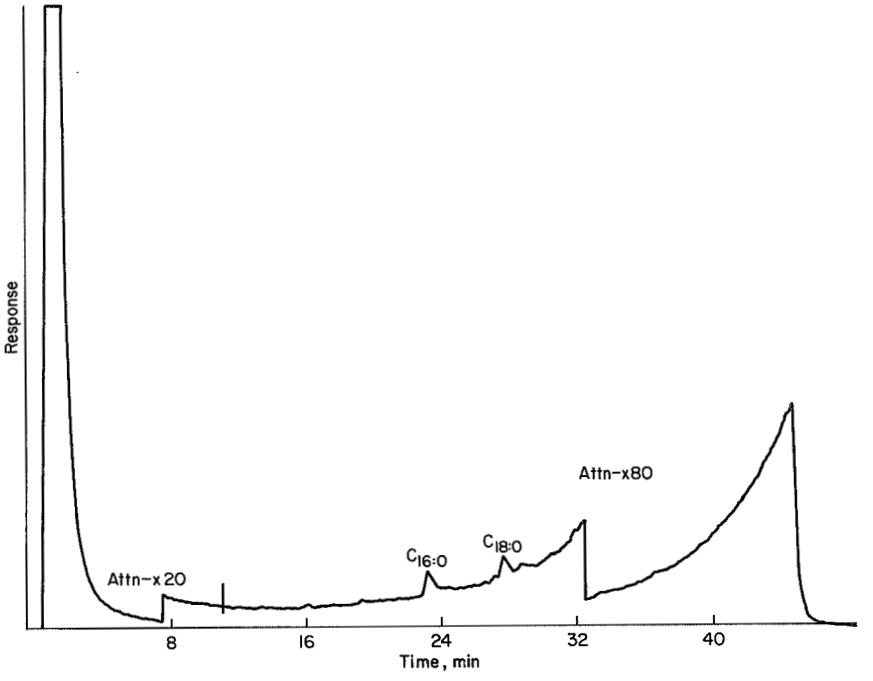
(c) Sand blank. Chromatographic conditions as on figure 28.

Figure 29 Continued.

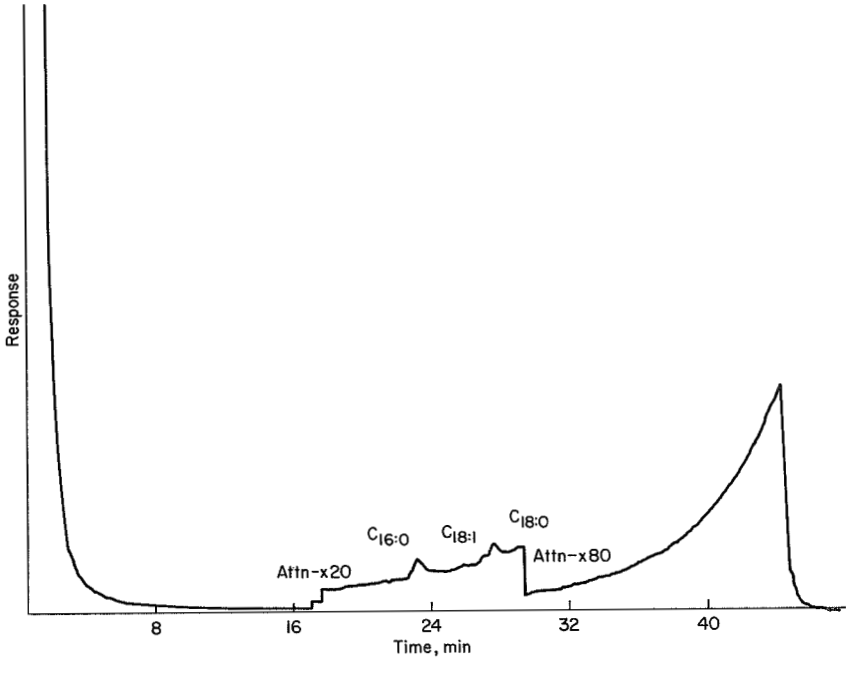


(d) Lunar sample. Chromatographic conditions as on figure 28.

Figure 29 Concluded.

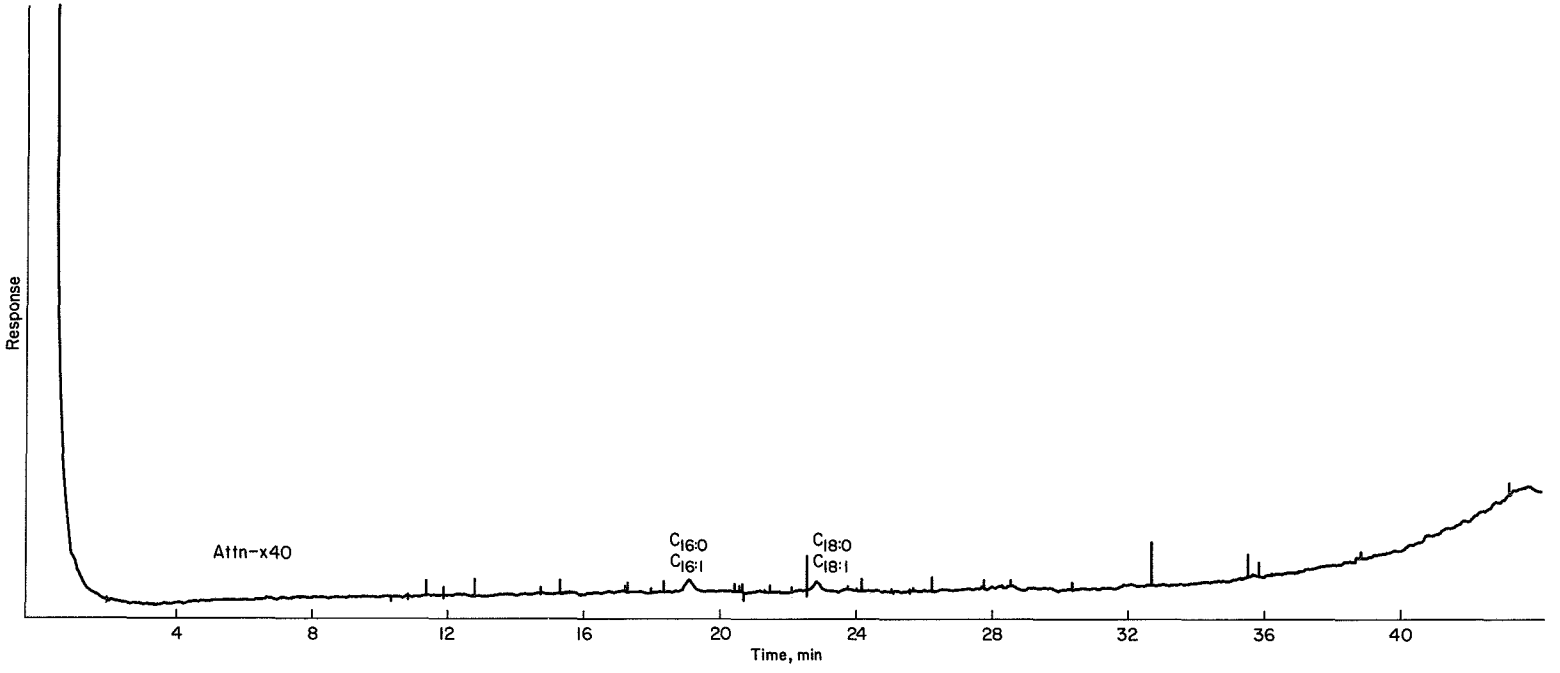


(a) Sand blank. Chromatographic conditions as on figure 27.



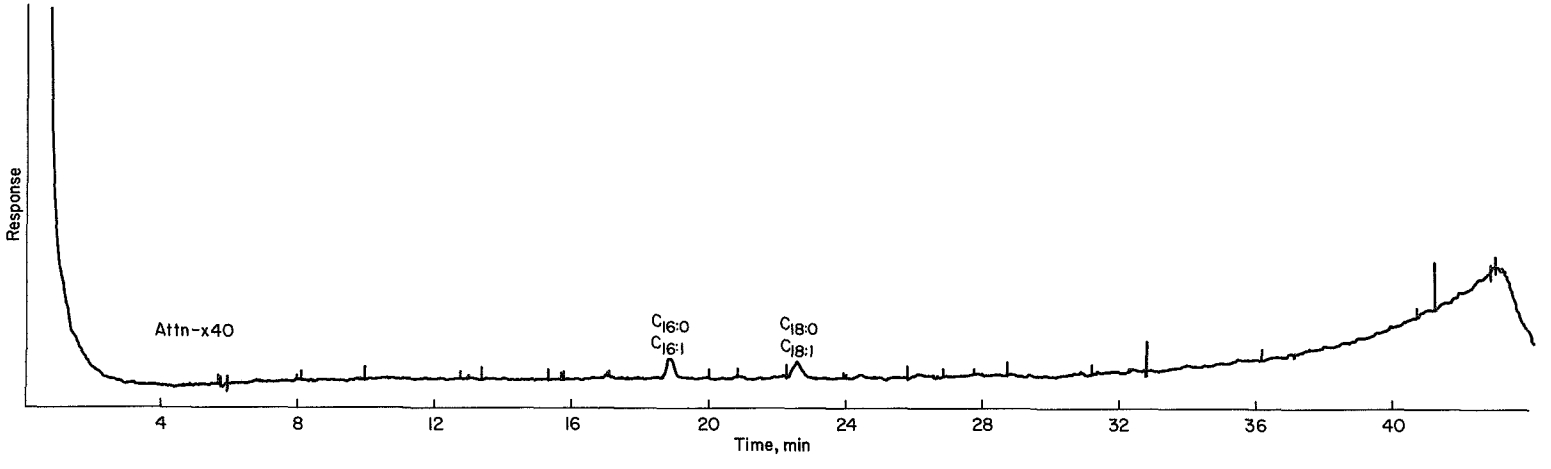
(b) Lunar sample. Chromatographic conditions as on figure 27.

Figure 30 Gas chromatograms of methyl esters of fatty acids from 10 percent of BF_3-methanol extract.



(c) Sand blank. Chromatographic conditions as on figure 28.

Figure 30 Continued.



(d) Lunar sample. Chromatographic conditions as on figure 28.

Figure 30 Concluded.

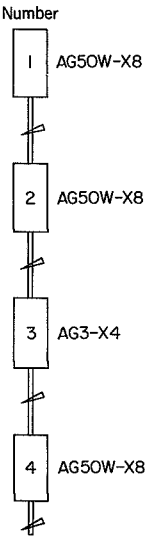


Figure 31 Ion exchange column assembly for carbohydrate study.

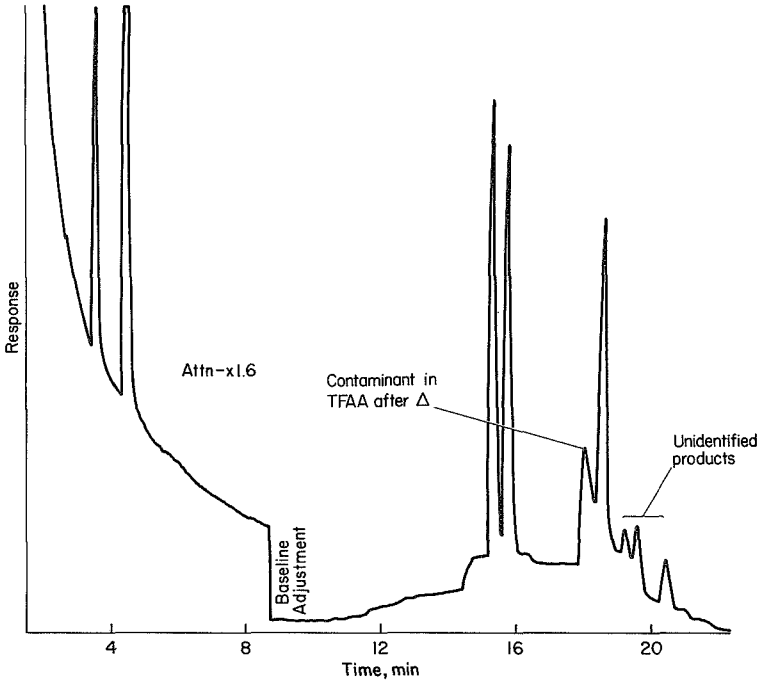


Figure 32 Recovery of monosaccharides using lunar analysis procedure. Chromatographic column, trifluoromethylpropylsilicone; temperature programmed from 140° to 175° C at 4°/min.

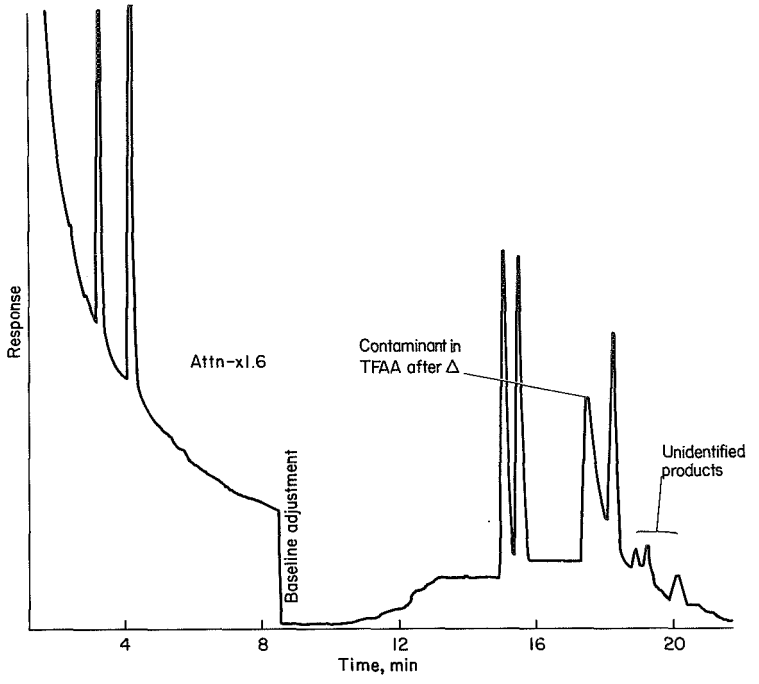


Figure 33 Trifluoroacetylation yields of standard monosaccharides. Column conditions as on figure 32.

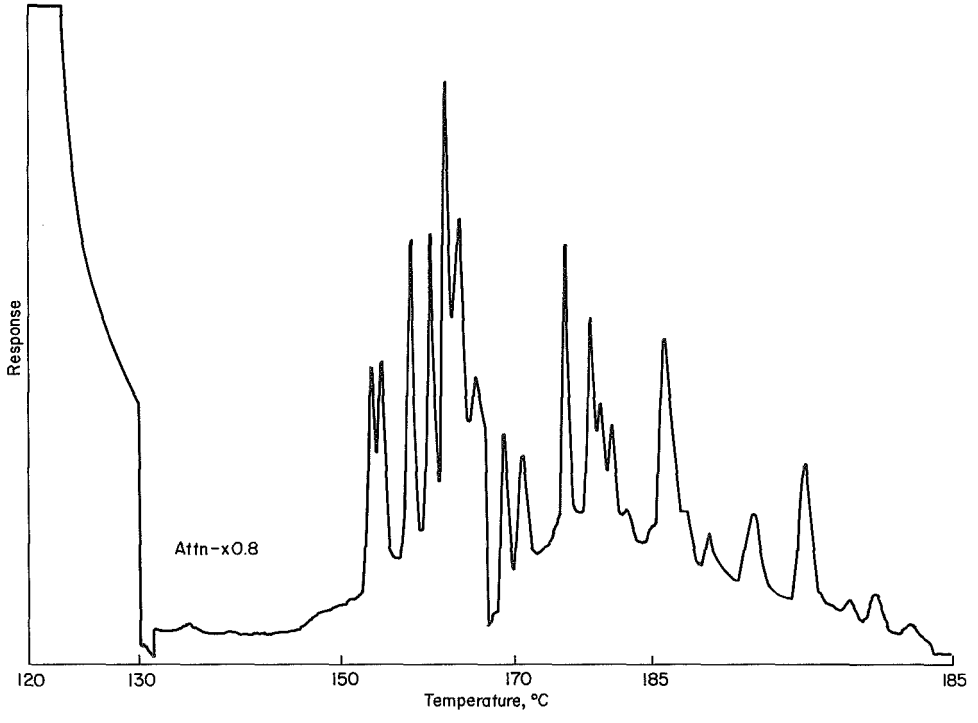
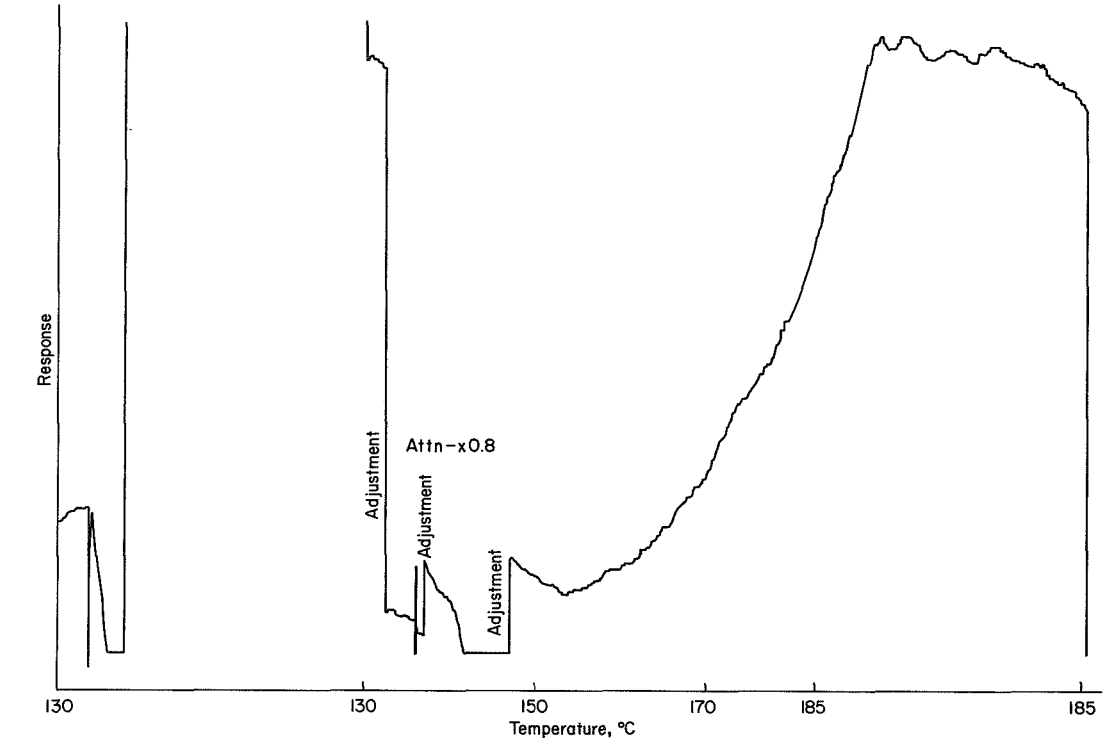
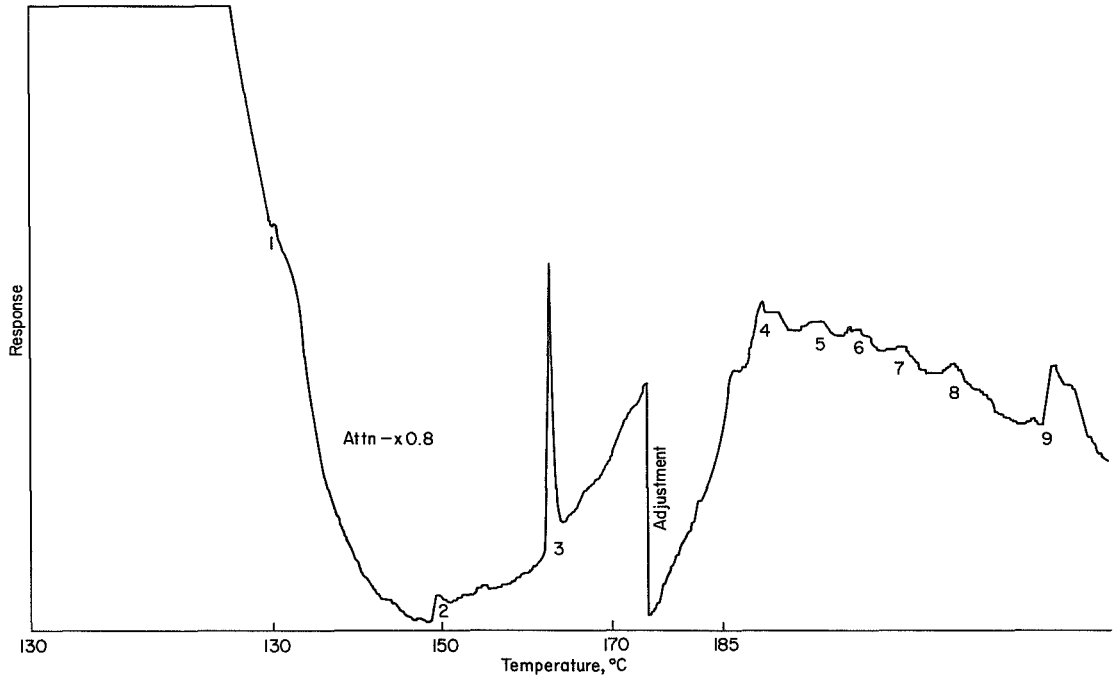


Figure 34 Trimethylsilylation yields from trimethylsilylation of standard monosaccharide mixture. Chromatographic column, neopentylglycol adipate; temperature programmed from 130° to 185° C at 4°/min.

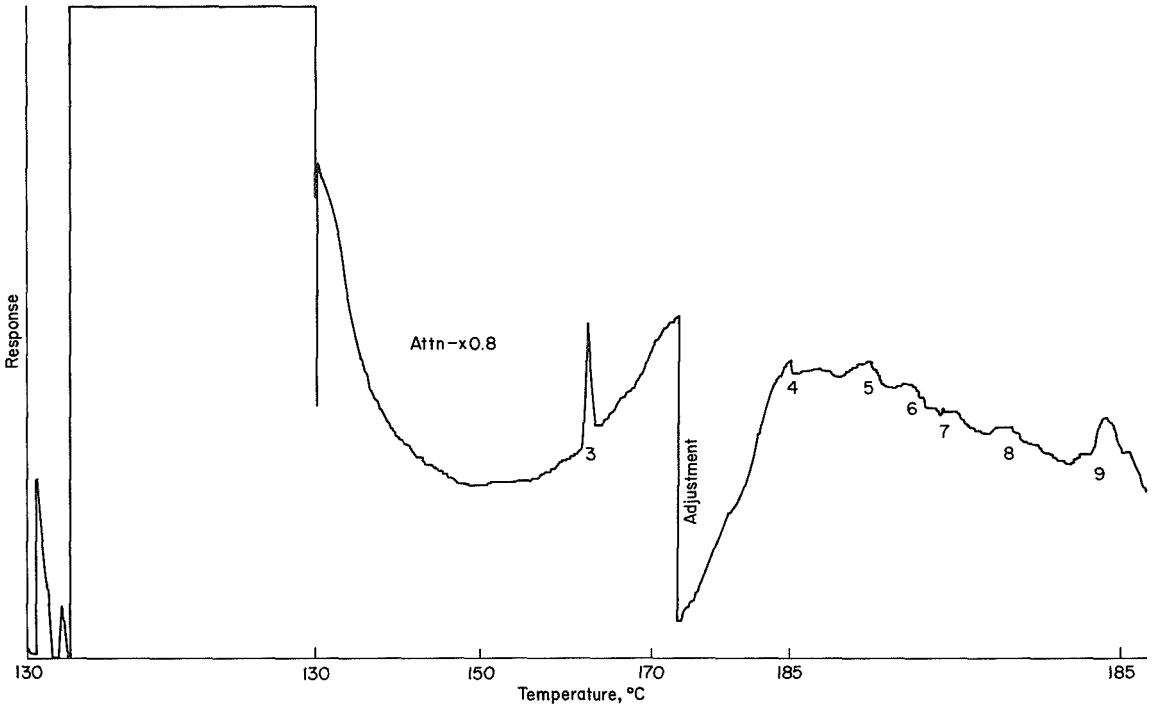


(a) Performance blank.



(b) Lunar sample.

Figure 35 Trimethylsilylation reaction. Column conditions as on figure 34.



(c) Sand blank.

Figure 35 Concluded.

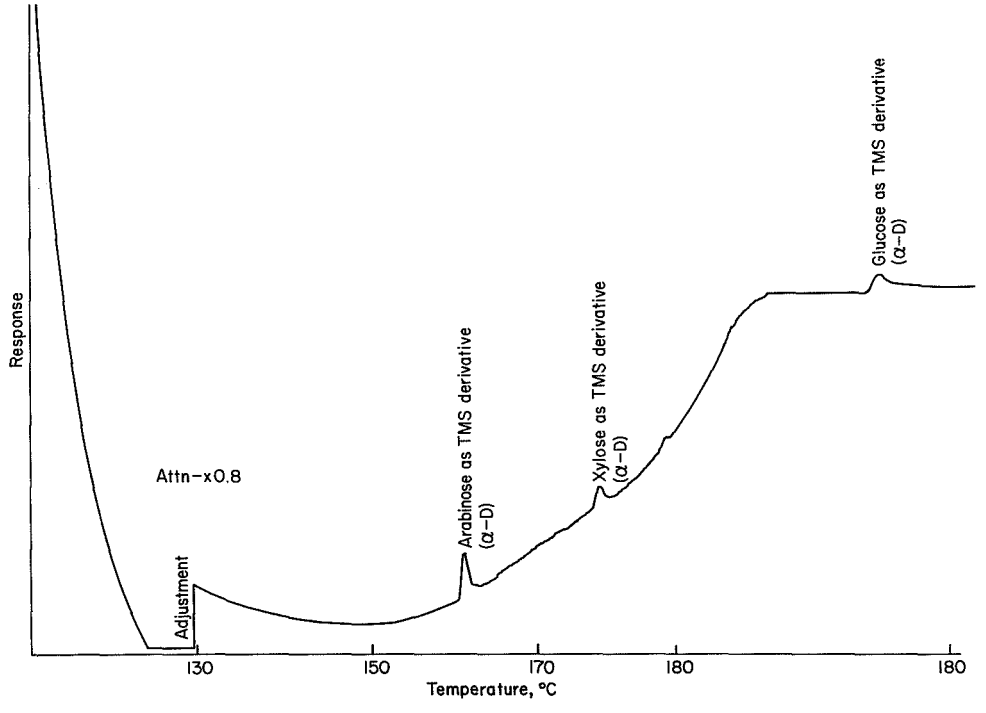
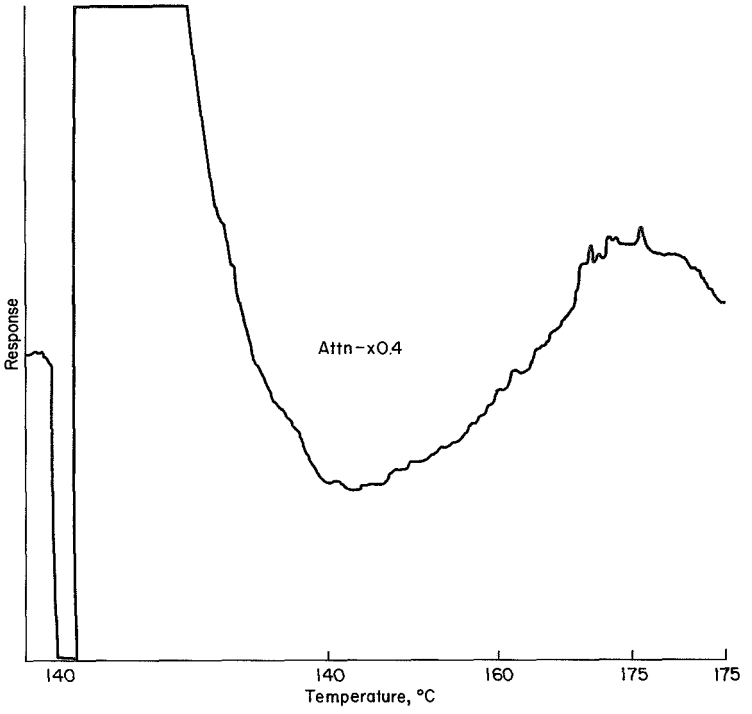
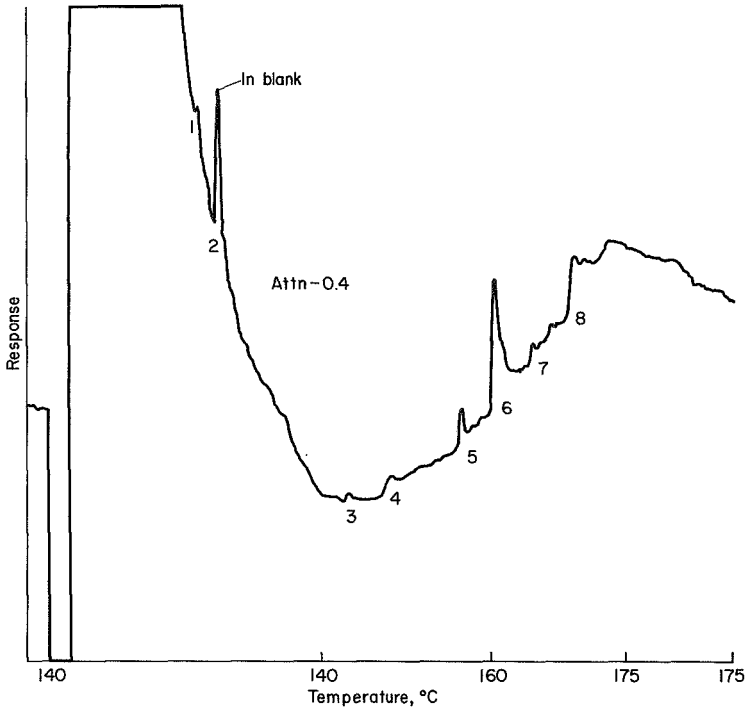


Figure 36 Detector response to 3 ng each of three standard monosaccharide TMS derivatives.

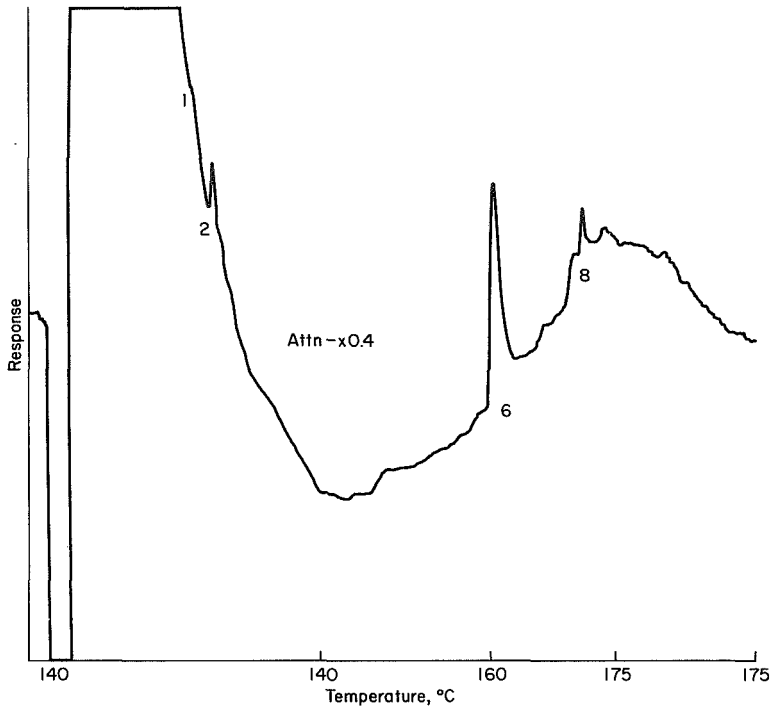


(a) Performance blank.

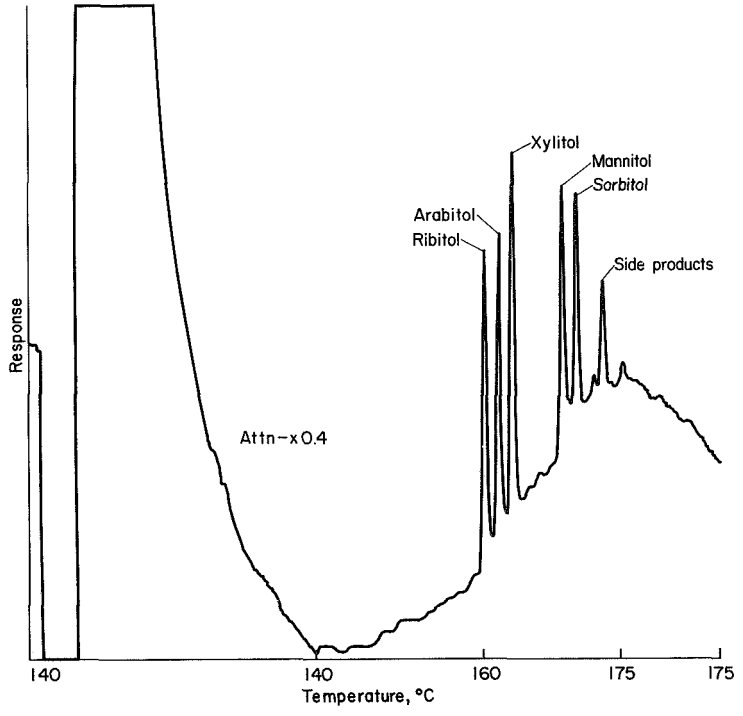


(b) Lunar sample (LSB).

Figure 37 Trifluoroacetylation reactions. Column conditions as on figure 32.

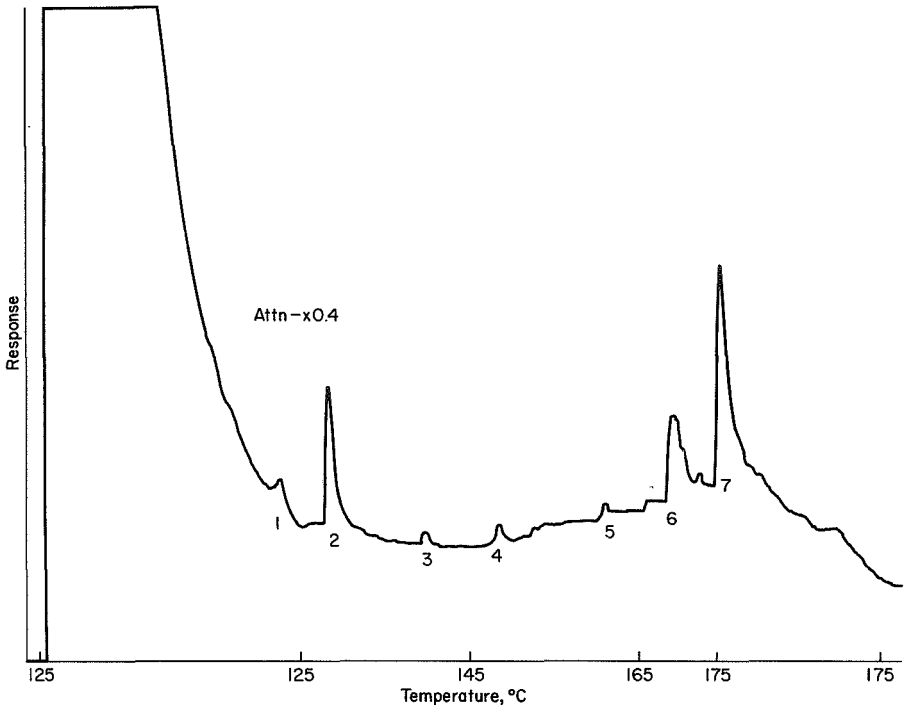


(c) Sand blank (LBB).

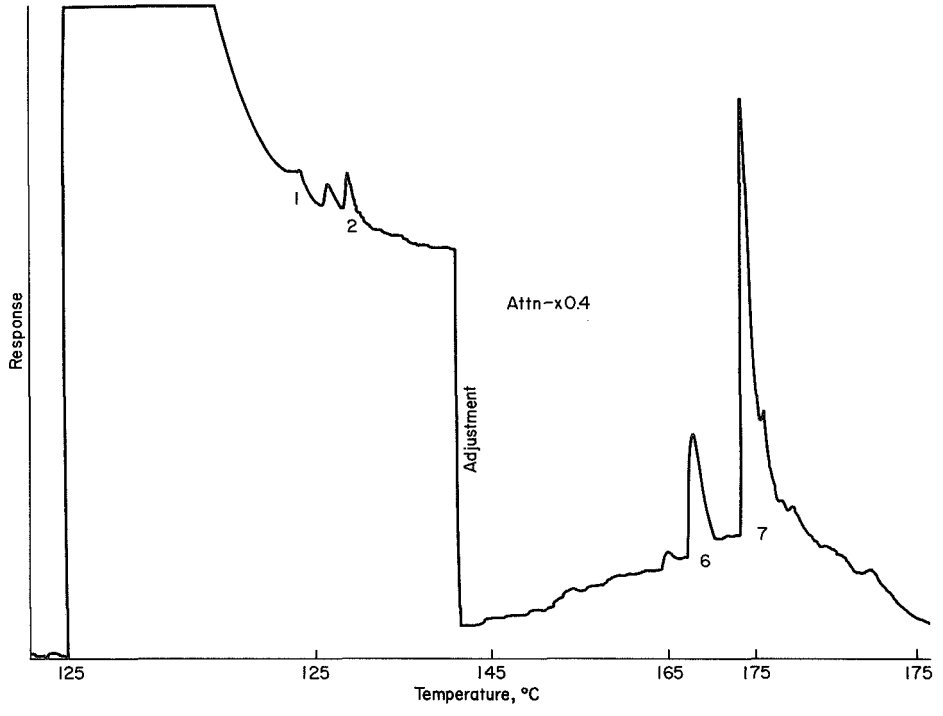


(d) Detector response to 50 ng each of five standard monosaccharide TFA derivatives.

Figure 37 Continued.



(e) Lunar sample (LSA). Temperature programmed from 125° to 175° C at 4°/min.



(f) Sand blank (LBA). Column condition as on (e) above.

Figure 37 Concluded.

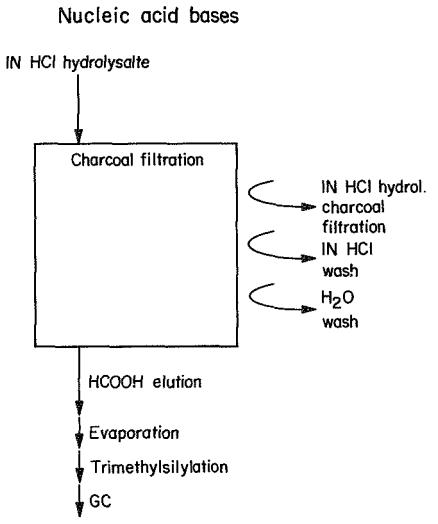


Figure 38 Scheme of analysis for nucleic acid bases.

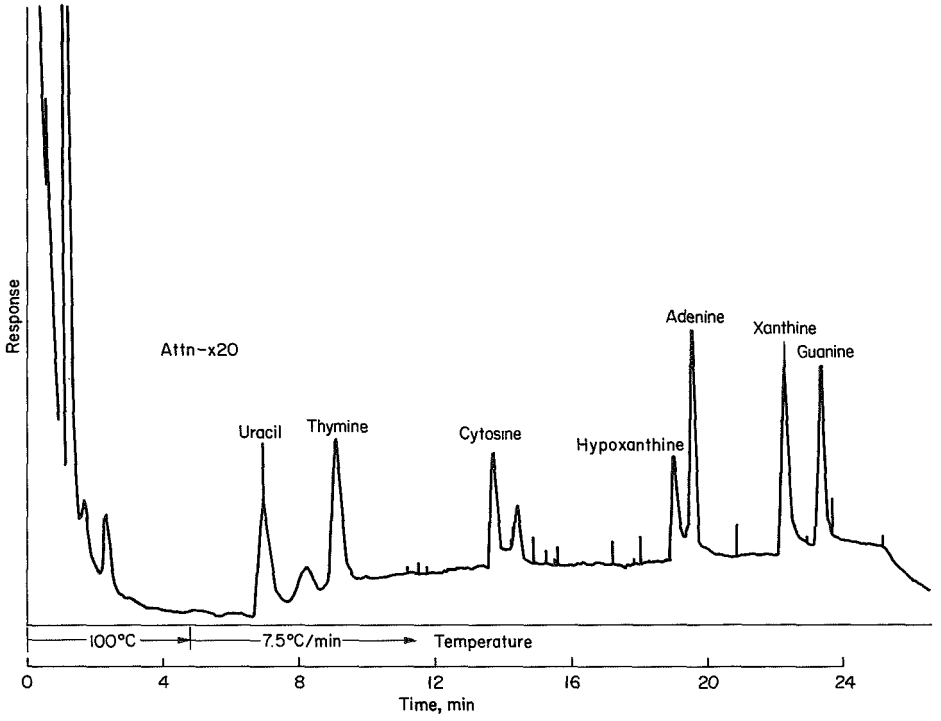


Figure 39 Gas chromatogram of derivatized nucleic acid bases (0.75 nmol each). Chromatographic column, 3 percent OV-17; temperature programmed from 100° to 300° C at 7.5°/min.

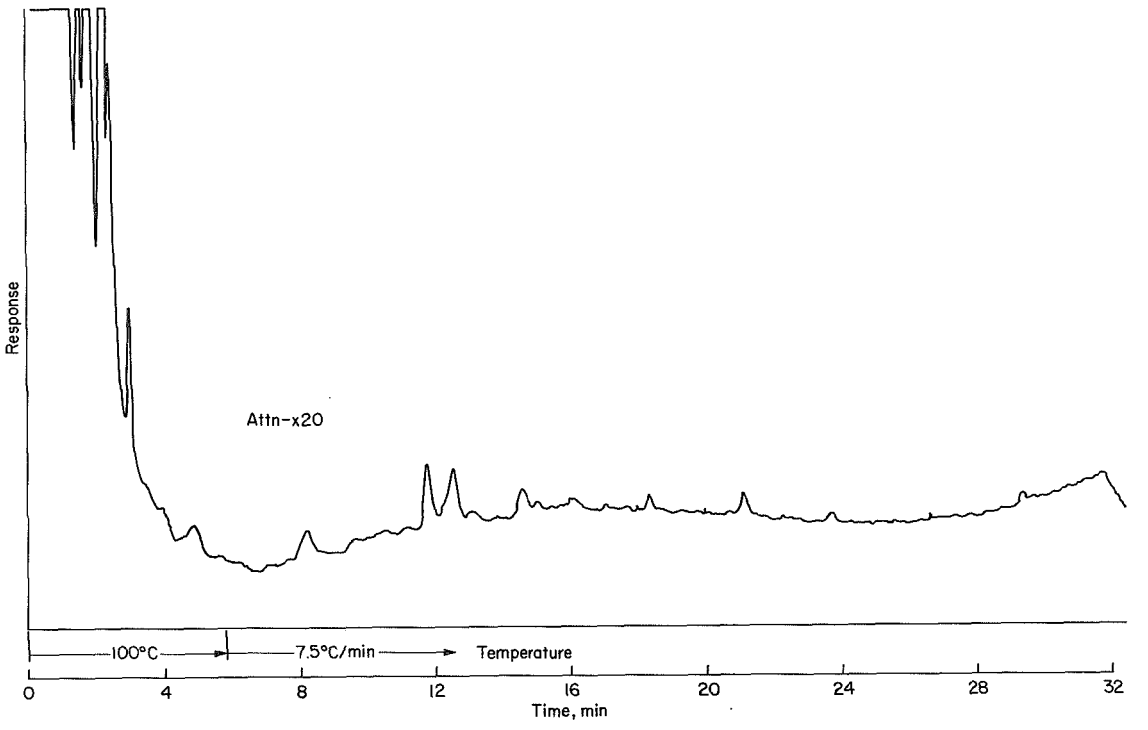


Figure 40 Gas chromatographic analysis of solvents and reagents taken through analytical scheme for nucleic acid bases. Chromatographic conditions as on figure 39.

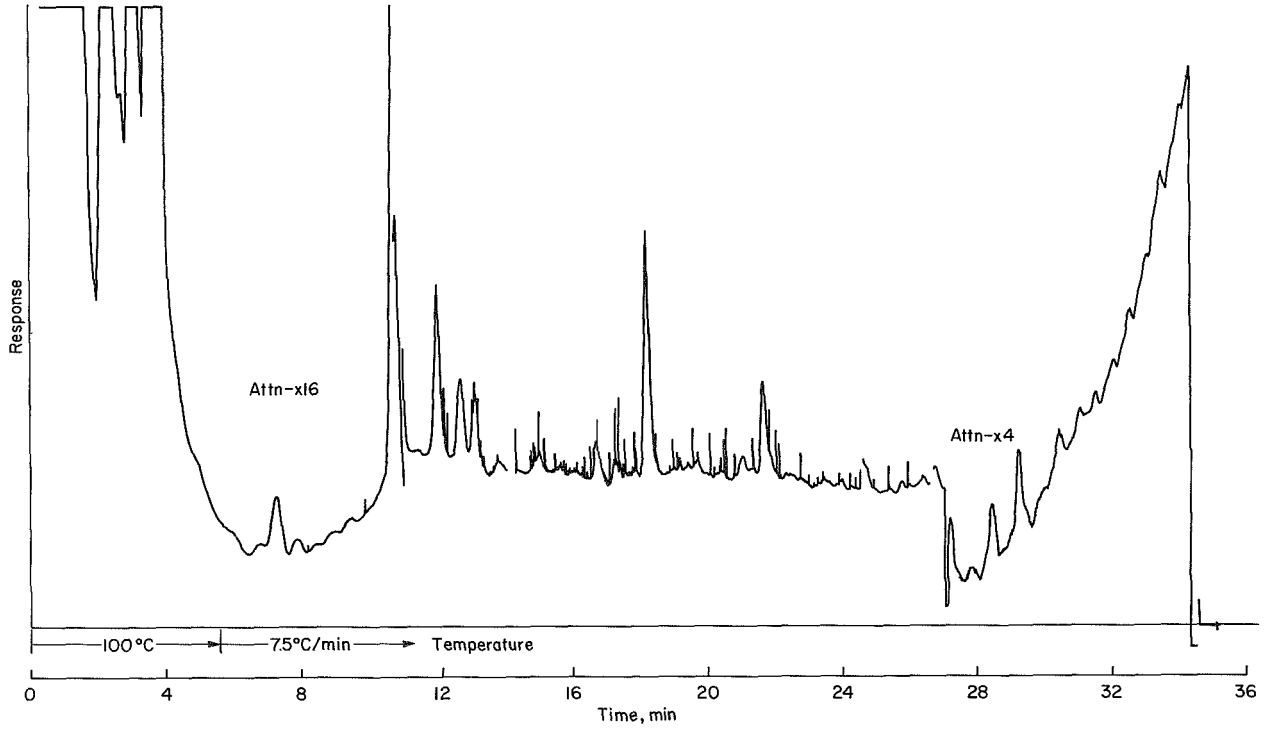


Figure 41 Gas chromatogram from extract of sand blank used in nucleic acid base analysis. Chromatographic conditions as on figure 39.

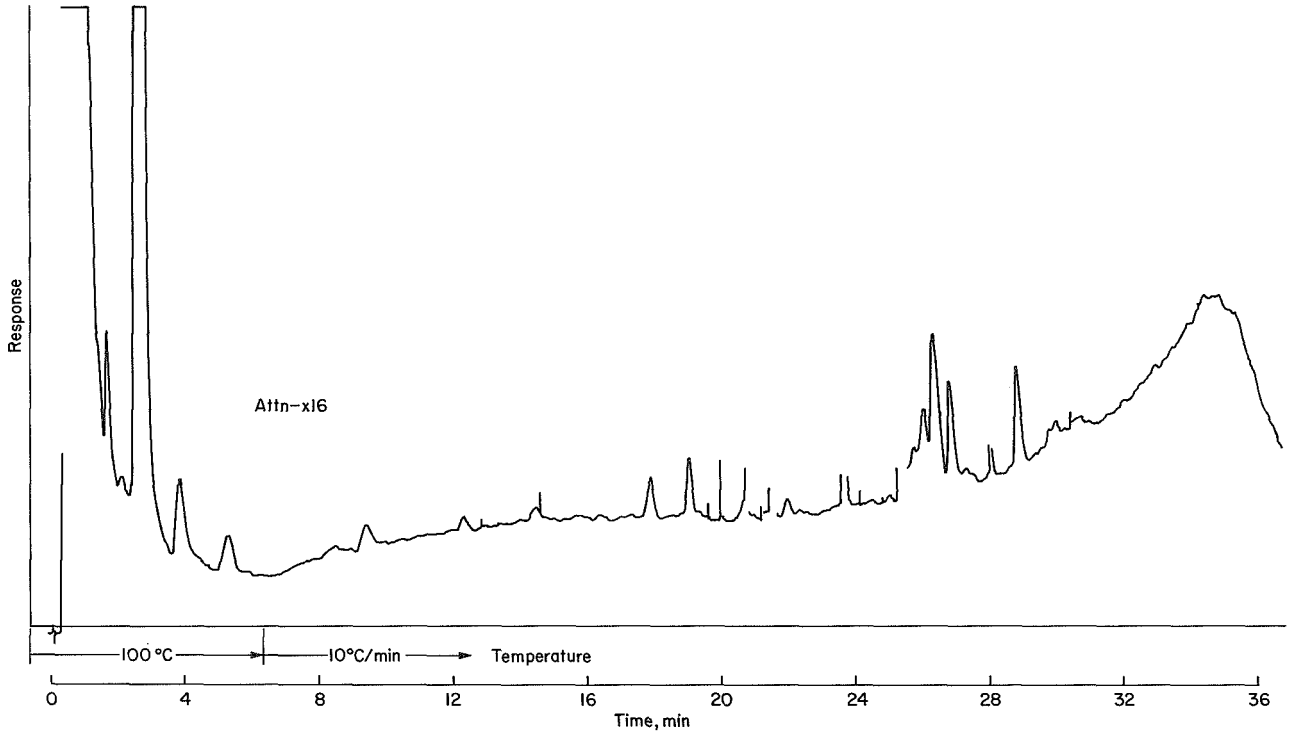


Figure 42 Gas chromatographic analysis of lunar sample for nucleic acid bases. Chromatographic conditons as on figure 39.

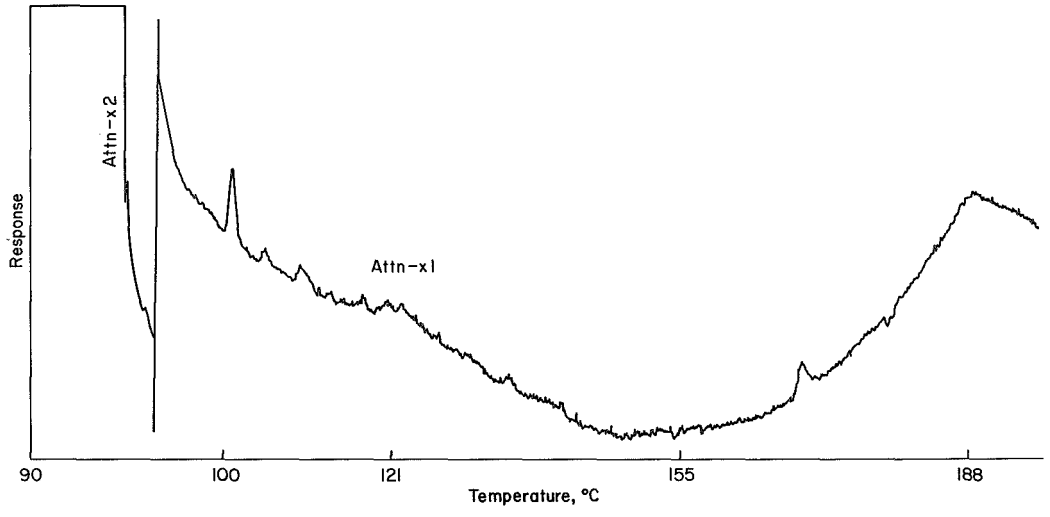
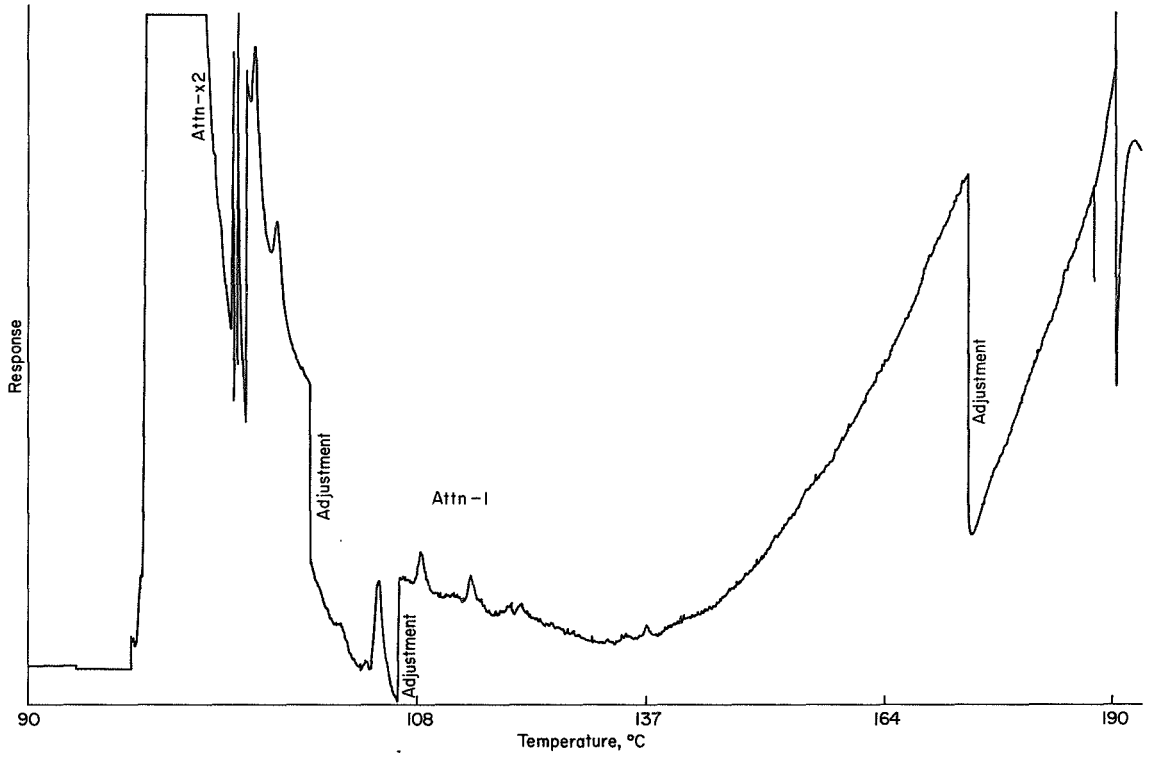
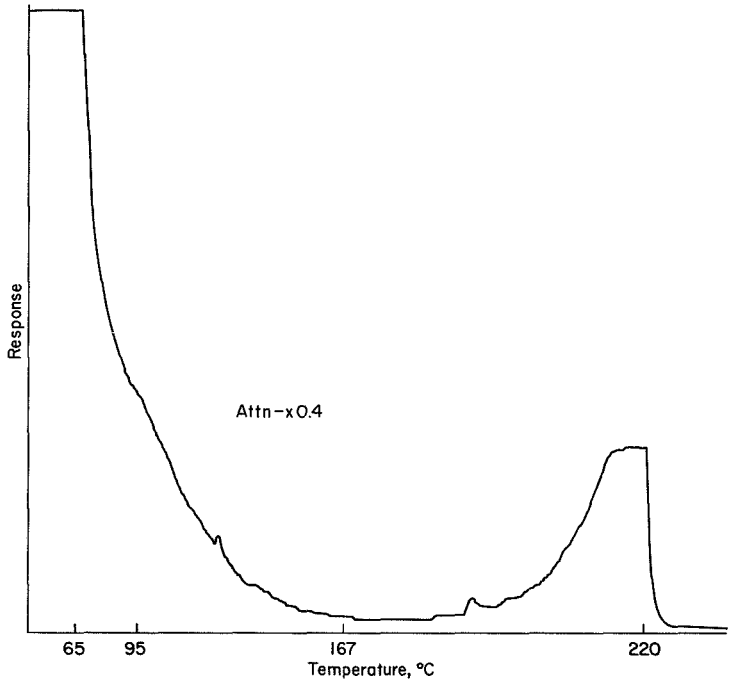


Figure 43 Gas chromatogram of derivatized benzene-methanol extract of lunar sample. Chromatographic column, 0.325 percent EGA; temperature programmed from 90° to 190° C at 4°/min.

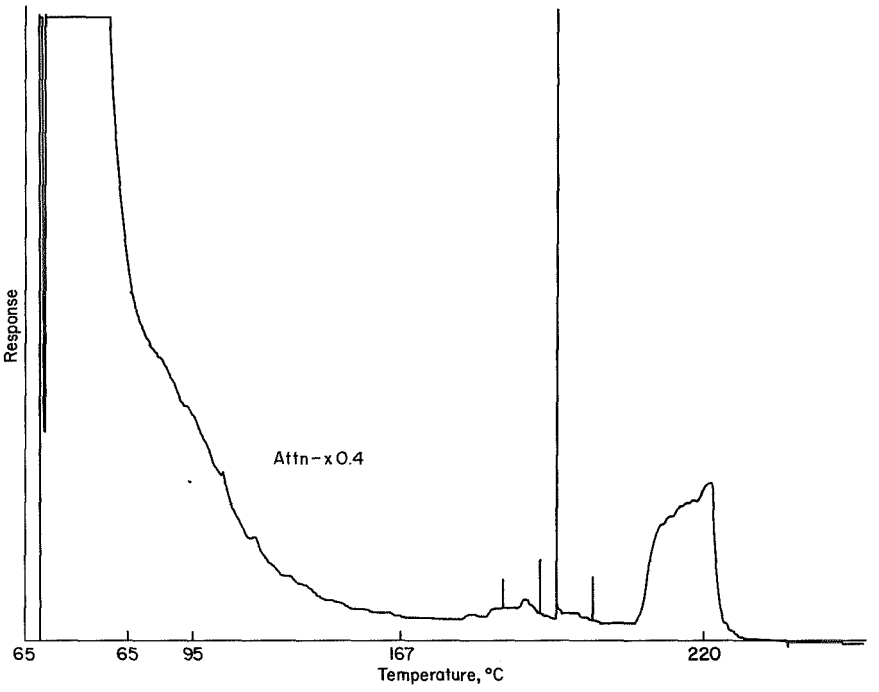


(a) Lunar sample not desalted. Chromatographic conditons as on figure 43.

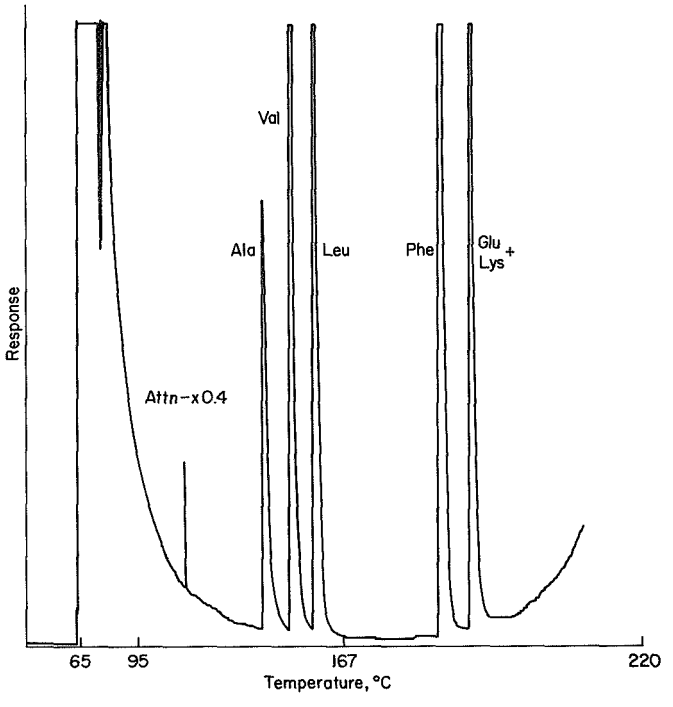


(b) Lunar sample (NH_4OH eluate). Chromatographic conditions, 3 percent OV-17; temperature programmed from 65° to 240° C at 6°/min.

Figure 44 Gas chromatograms of water extract.

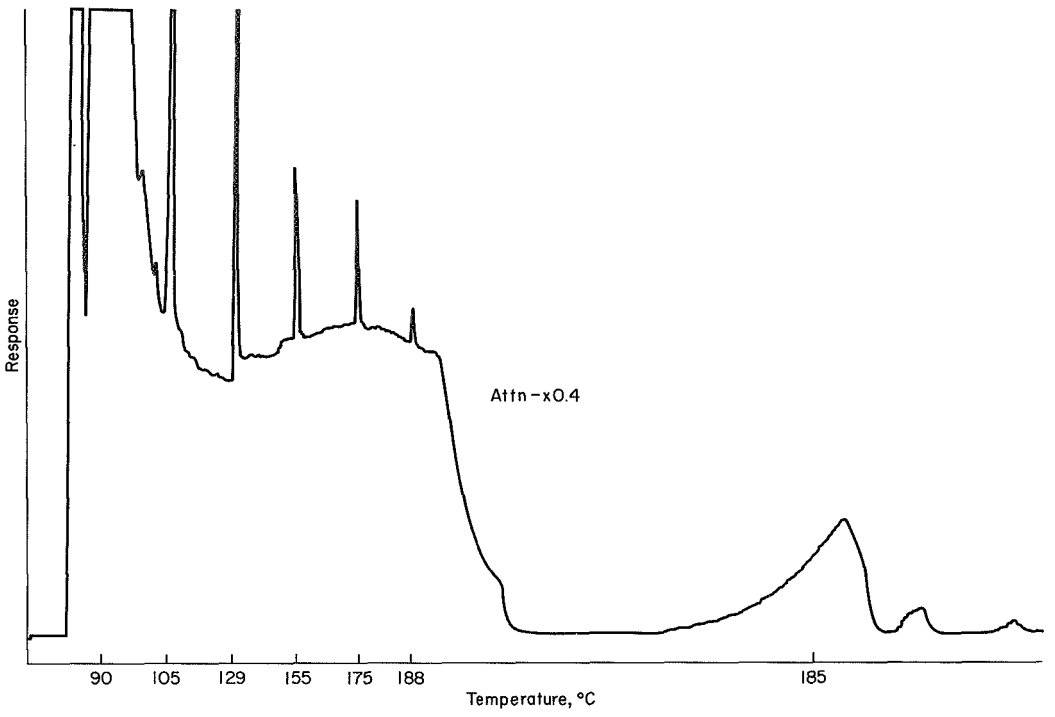


(c) Sand blank (NH_4OH eluate). Chromatographic conditons as on (b) above.

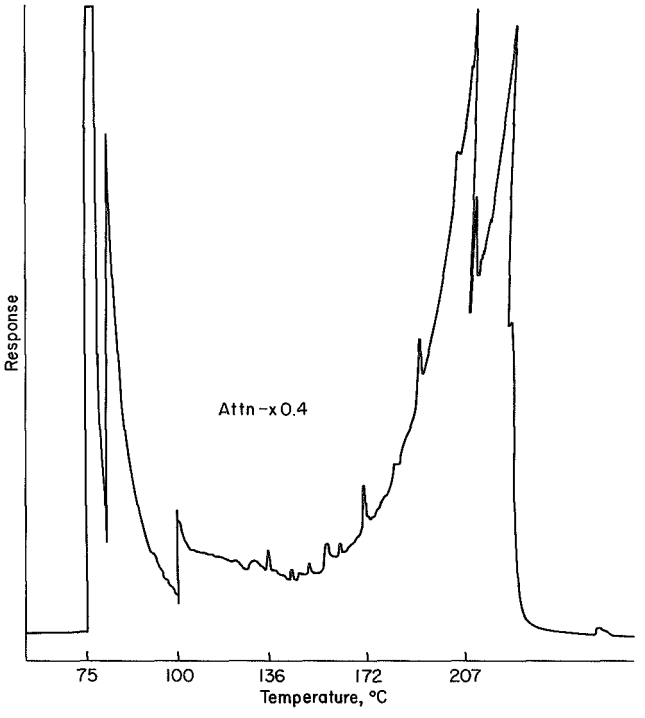


(d) Sensitivity check, amino acid derivative standard, 10 ng each of alanine, valine, leucine, phenylalanine, glutamic acid, and lysine. Chromatographic conditions as on (b) above.

Figure 44 Concluded.

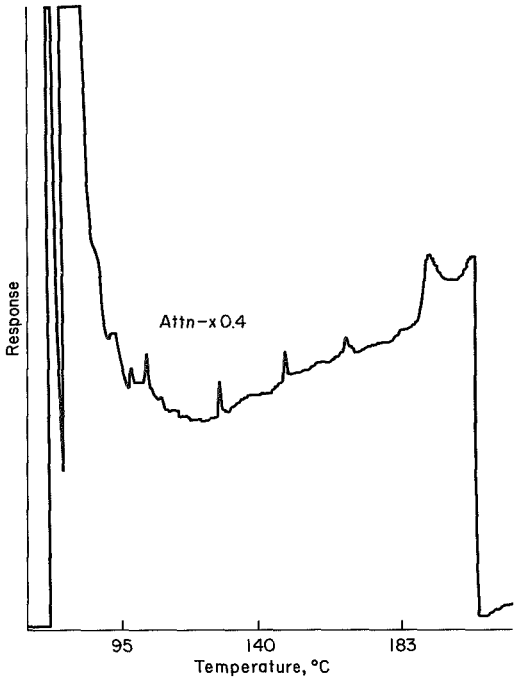


(a) Lunar sample, esterified and acylated.

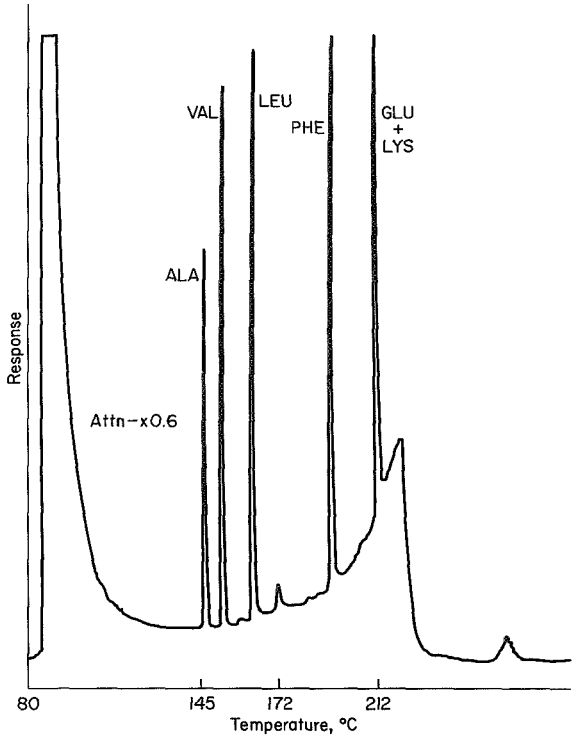


(b) Lunar sample, acylated.

Figure 45 Gas chromatograms of 1N HCl hydrolysate. Chromatographic conditions as on figure 43.

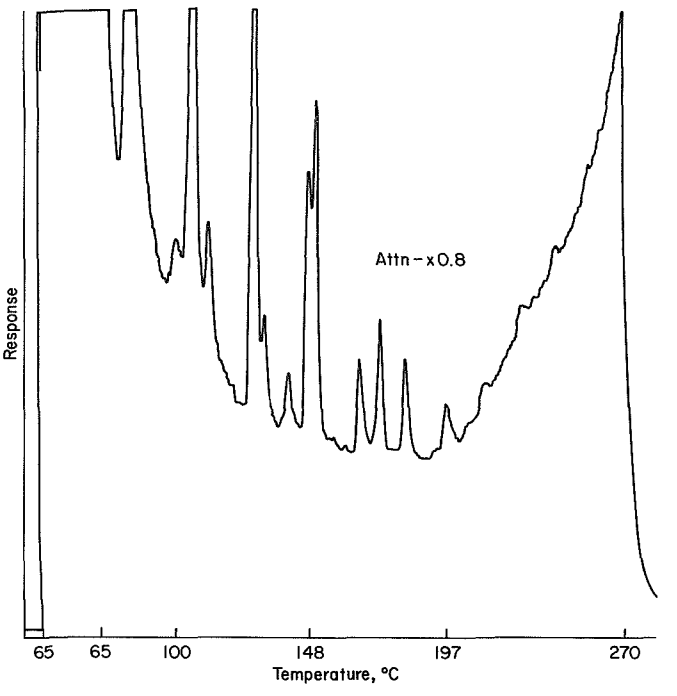


(c) Lunar sample, esterified.

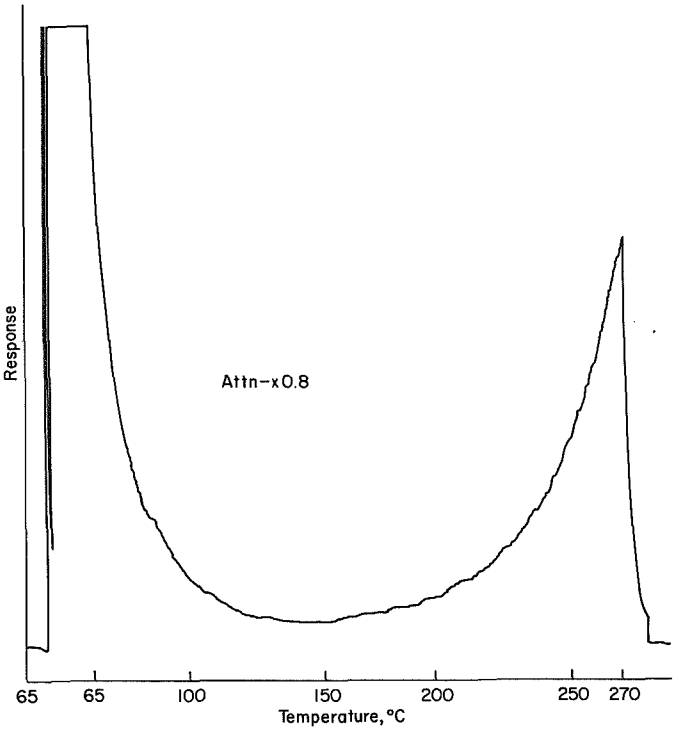


(d) Performance standard.

Figure 45 Concluded.

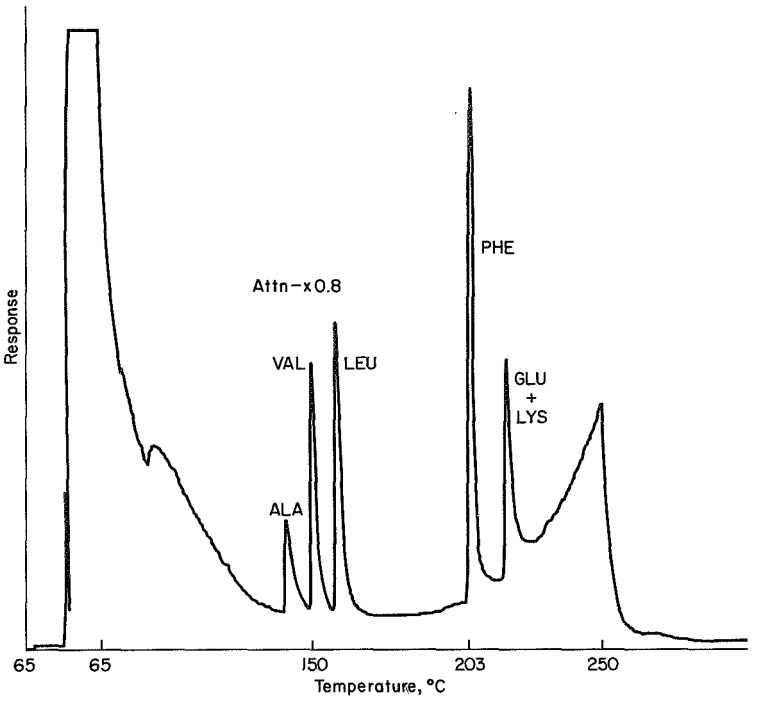


(a) Lunar sample.



(b) Sand blank.

Figure 46 Gas chromatograms of 1N HCl hydrolysis. Chromatographic column, 3 percent OV-17; temperature programmed from 65° to 240° C at 4°/min.



(c) Performance standard.

Figure 46 Concluded.

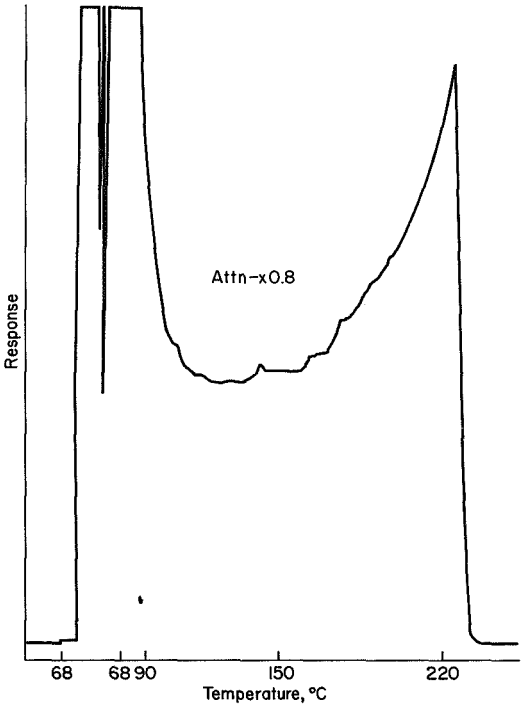


Figure 47 Gas chromatogram of 1N HCl hydrolysate of material from trap E of rocket exhaust tests. Chromatographic conditions as on figure 43 except programmed initially at 68° C.

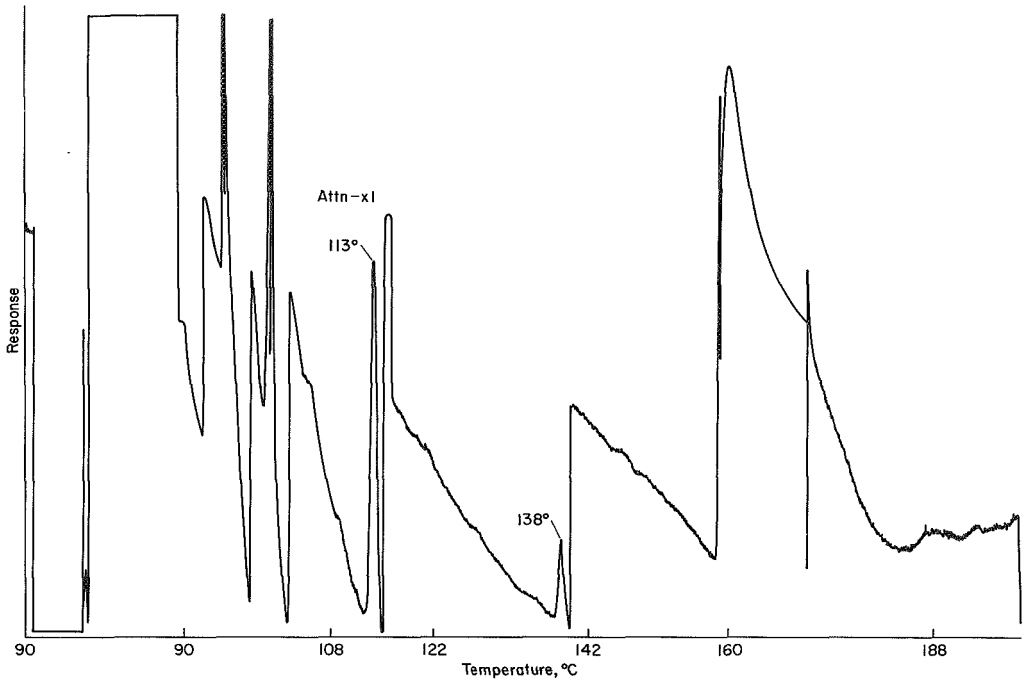
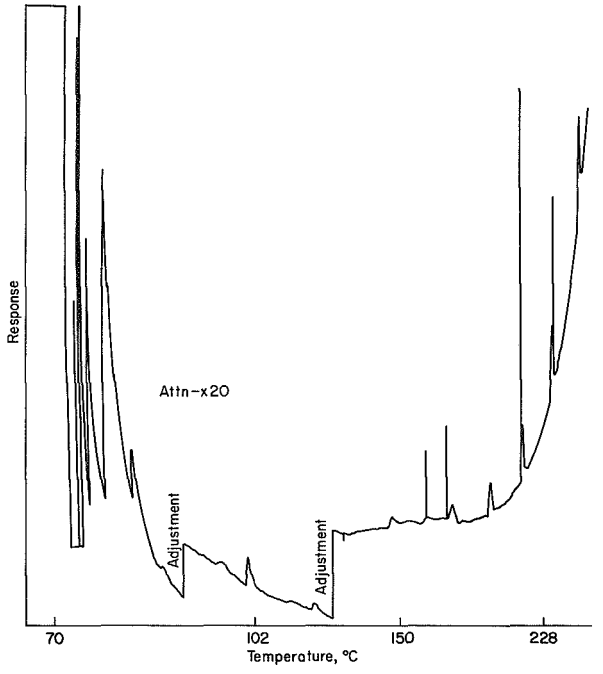
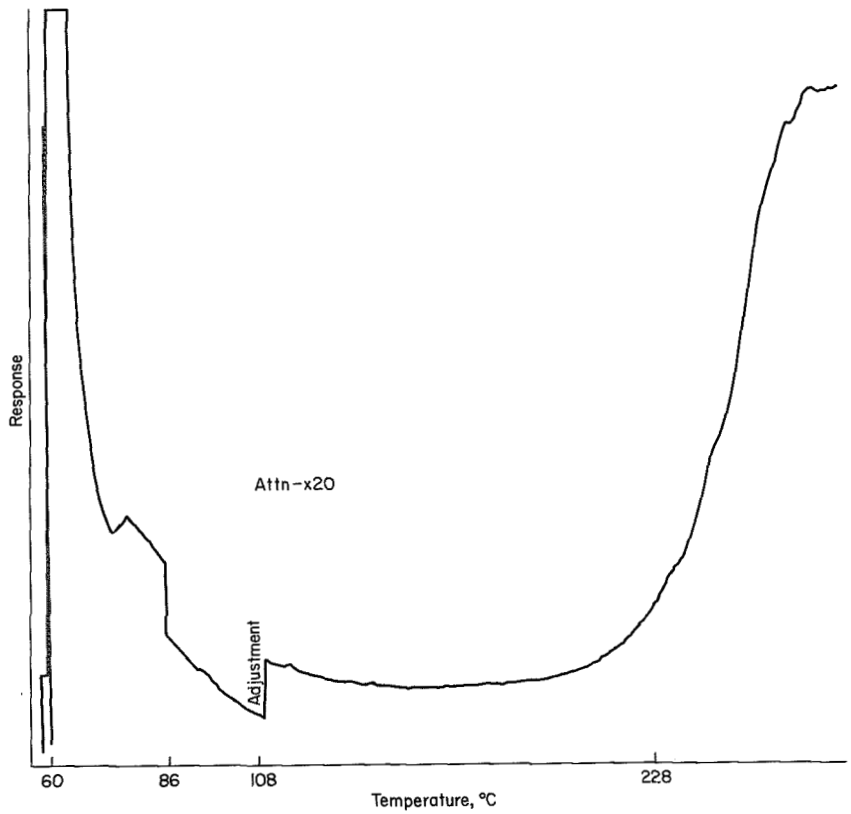


Figure 48 Gas chromatogram of derivatized 6N HCl hydrolysates of lunar sample. Chromatographic conditions as on figure 43.

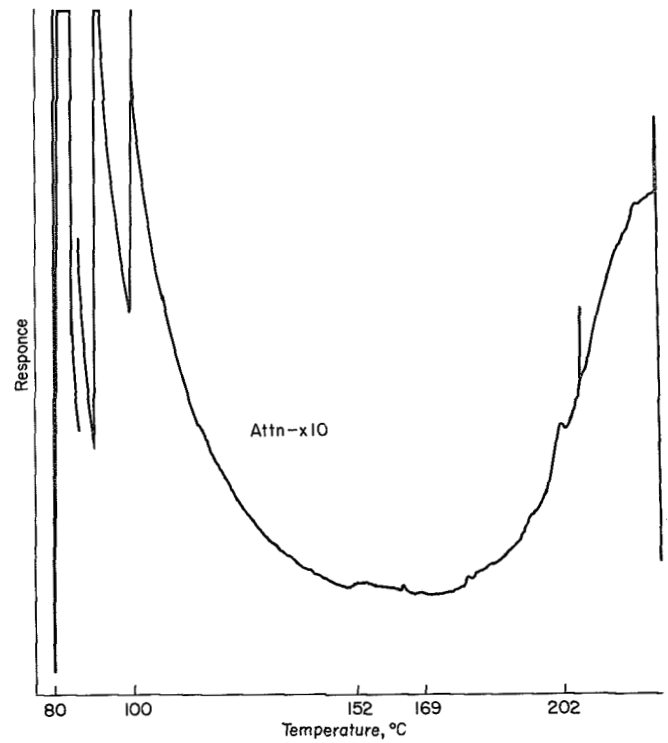


(a) Reagent blank. Chromatographic conditions same as figure 46(a) except programmed from 70° C at 4°/min.

Figure 49 Gas chromatograms.

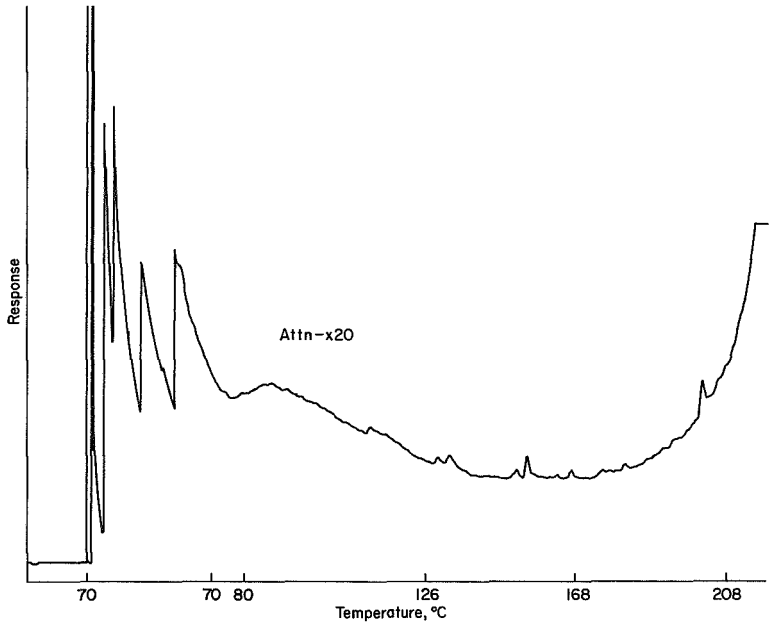


(b) Column blank. Chromatographic conditions as on *figure 46(a) except* programmed from 80° C.

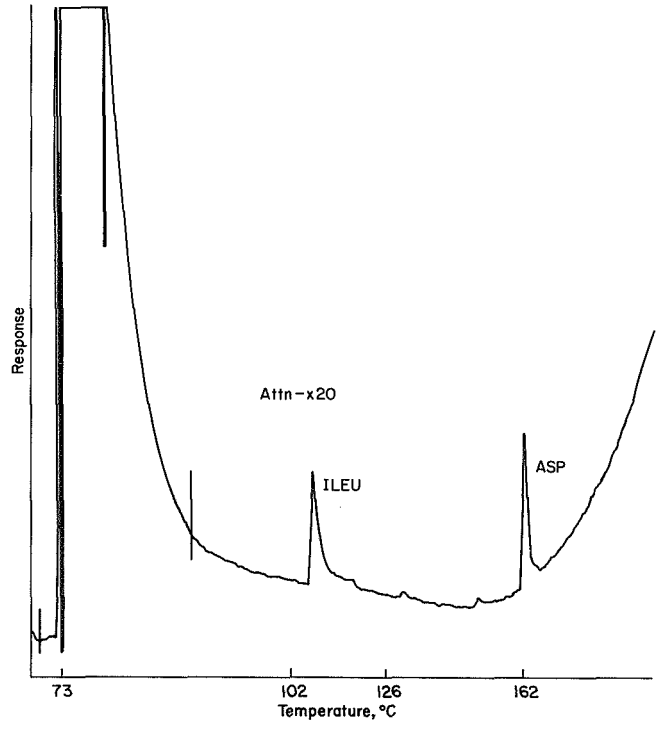


(c) 1N HCl hydrolysis of sand blank. Chromatographic conditions as on (b) above.

Figure 49 Continued.

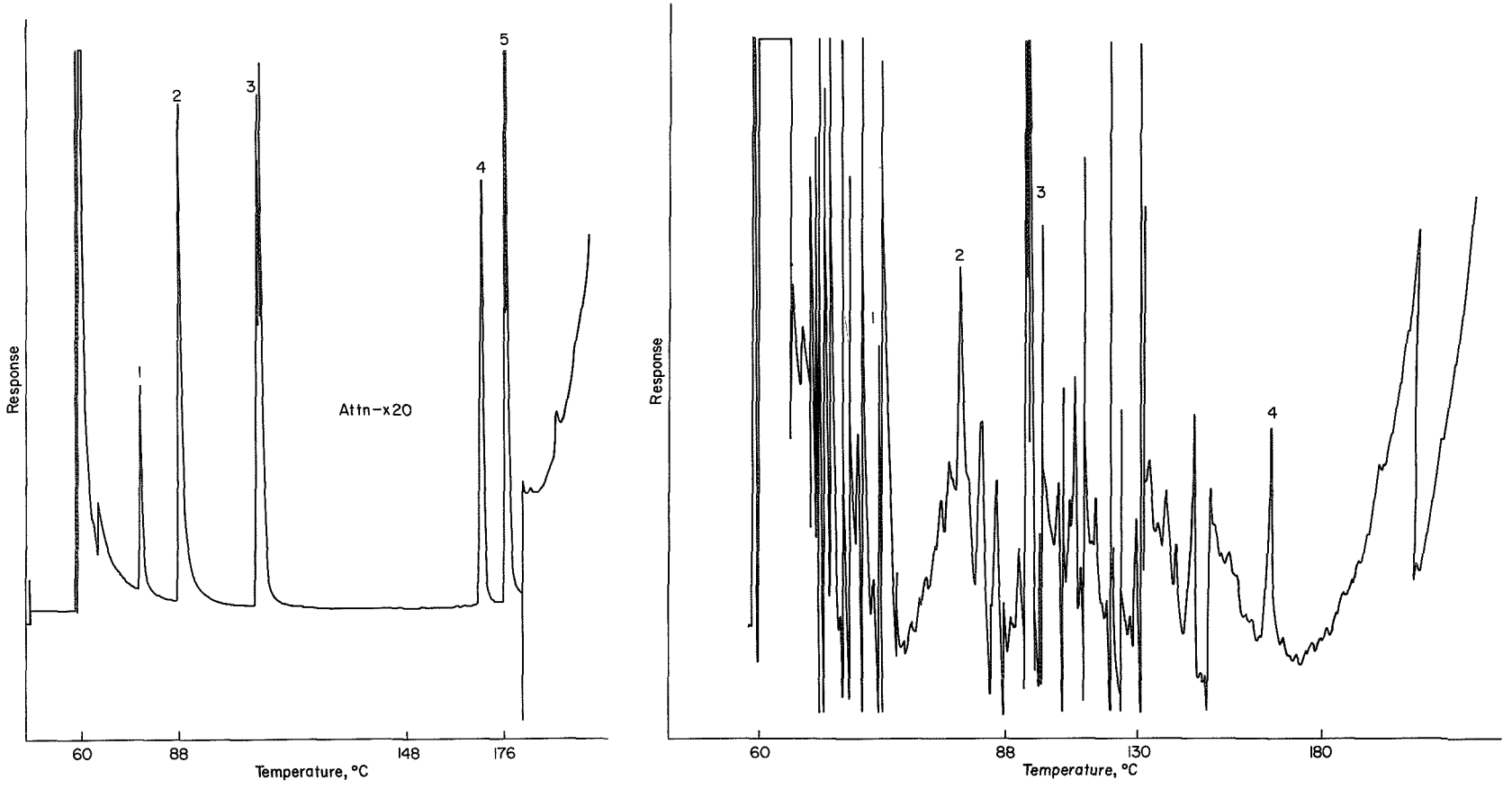


(d) Sand blank and ion exchange blank. Chromatographic conditions as on (a) above.



(e) Sensitivity check, 40 ng each of isoleucine and aspartic acid. Chromatographic conditions as on figure 46(a) except programmed from 75° C.

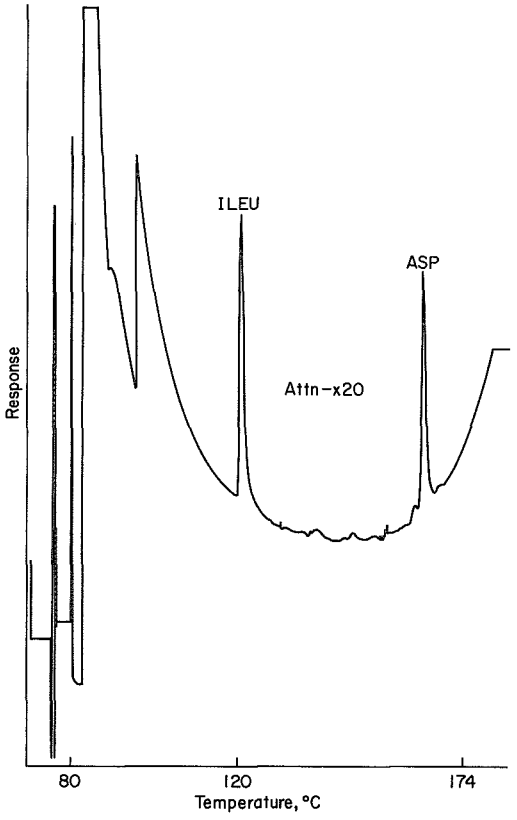
Figure 49 Concluded.



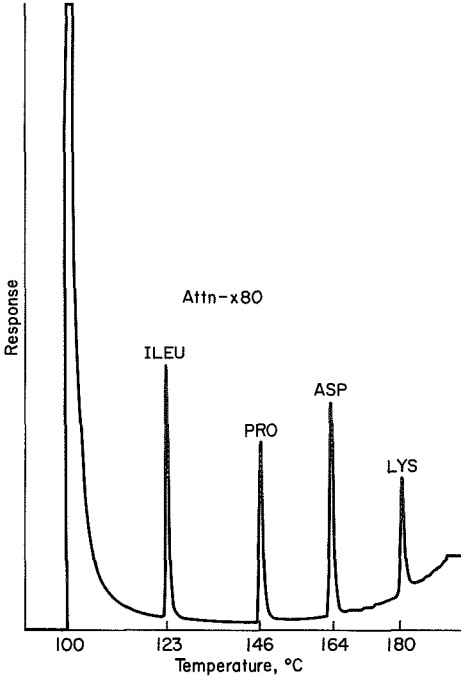
(a) Derivatization standard: 1 = octanol, 2 = hexylamine, 3 = valine, 4 = lauric acid, 5 = adipic acid.

(b) Derivatized standard added to 1N HCl hydrolysate of lunar sample.

Figure 50 Gas chromatograms. Chromatographic conditions as on figure 46(a) except programmed from 60° C.

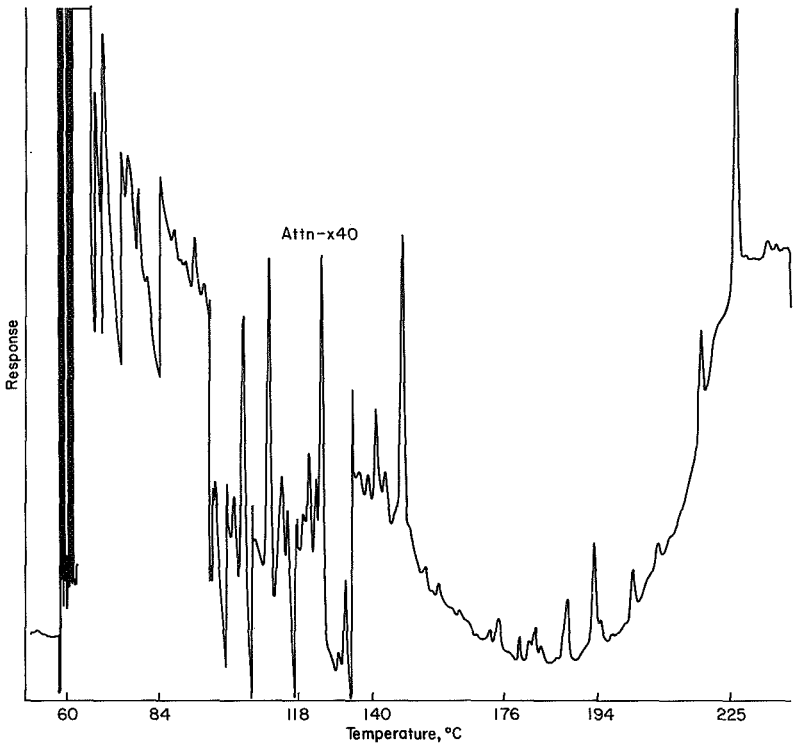


(a) 10 ng each of isoleucine and aspartic acid. Chromatographic conditions as on figure 49(b).

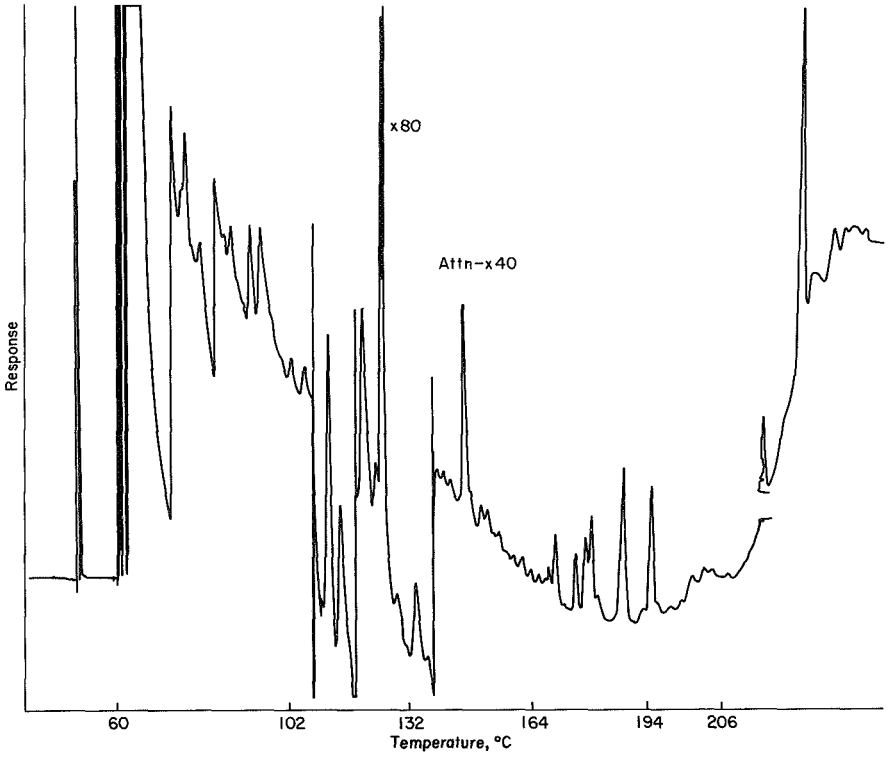


(b) 100 ng each of isoleucine, proline, aspartic acid, and lysine. Chromatographic conditions as on figure 46(a) except programmed from 100° C at 4°/min.

Figure 51 Gas chromatograms of derivatized amino acid standard.

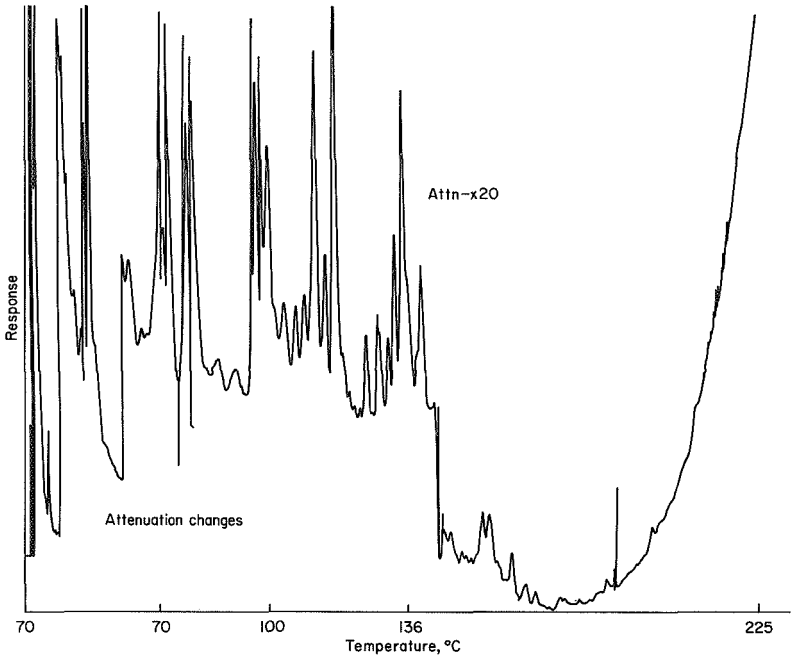


(a) Lunar sample.

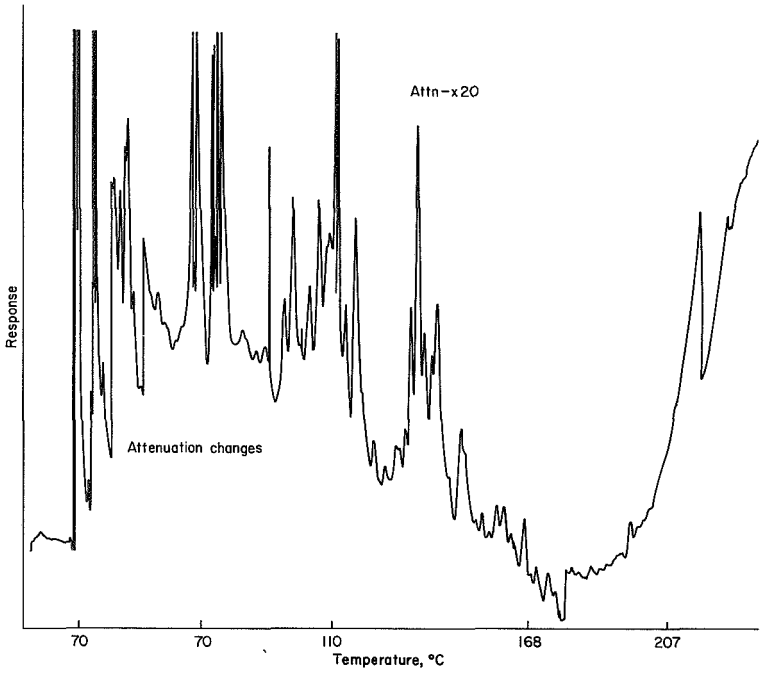


(b) Pueblito de Allende meteorite sample.

Figure 52 Gas chromatograms of derivatized 1N HCl hydrolysate. Chromatographic conditions same as figure 50(a).

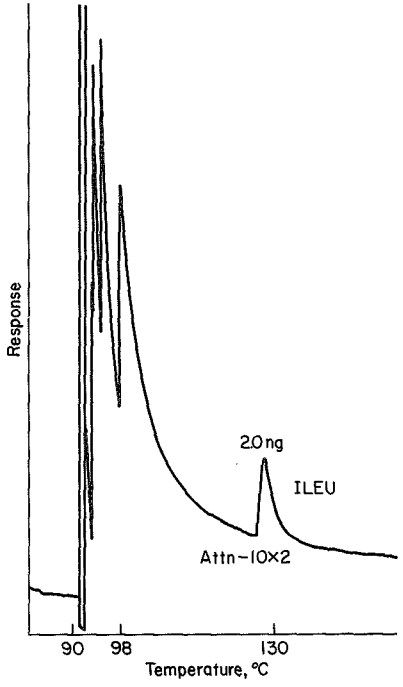


(a) Derivatized pentane extract of 6N HCl hydrolysate of lunar sample. Chromatographic conditions as on figure 49(a) except initial temperature at 70° C held for 8 min.

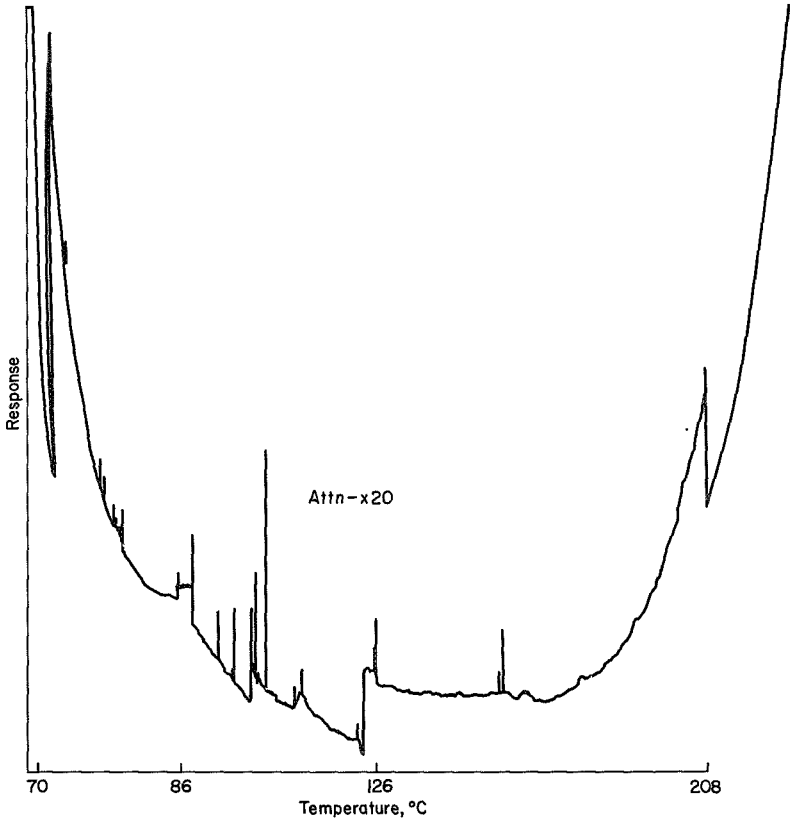


(b) Derivatized pentane extract of 1N HCl hydrolysate of Pueblito de Allende meteorite. Chromatic conditions as on (a) above.

Figure 53 Gas chromatograms.

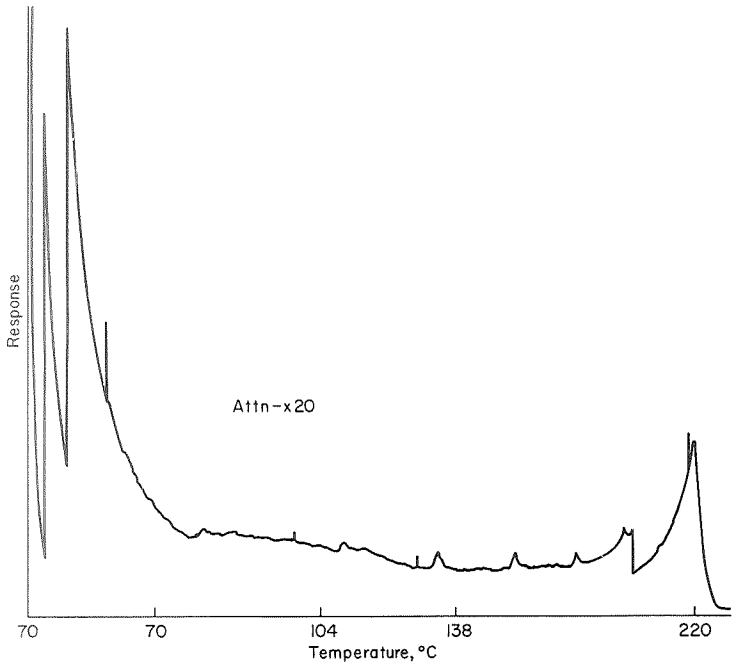


(c) Sensitivity check, 2.0 ng of isoleucine. Chromatographic conditions as on figure 46(a) except programmed from 90° C.



(d) Pentane solvent esterified but not acylated. Chromatographic conditions as on (a) above.

Figure 53 Continued.



(e) Pentane solvent esterified and acylated. Chromatographic conditions as on (a) above.

Figure 53 Concluded.

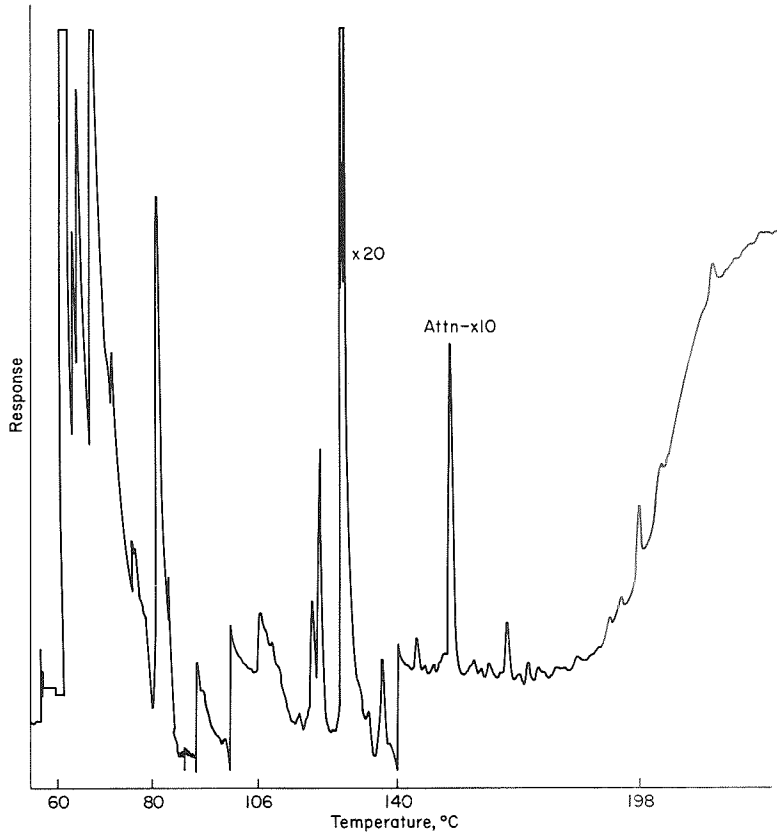
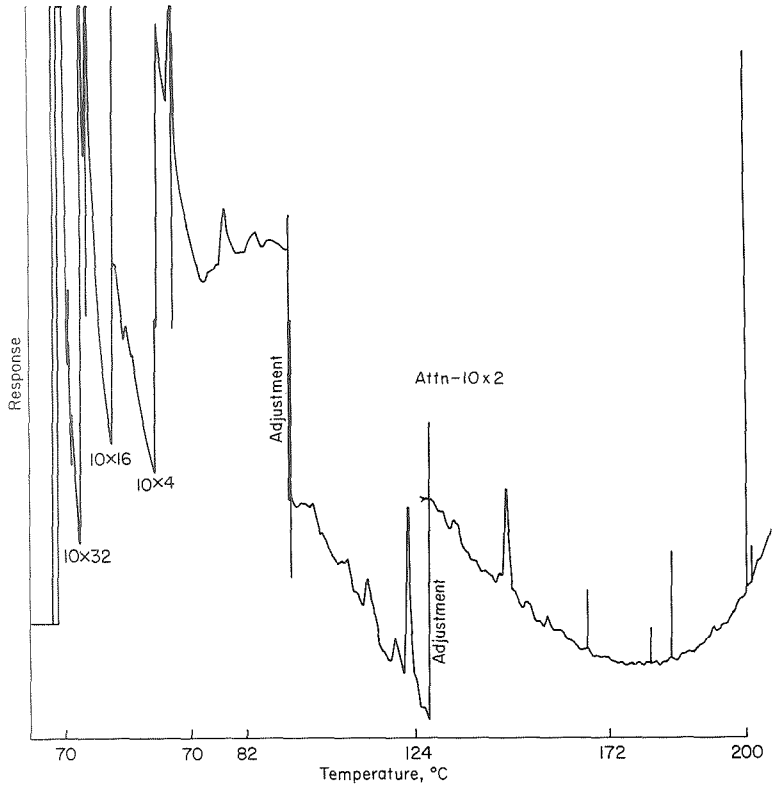
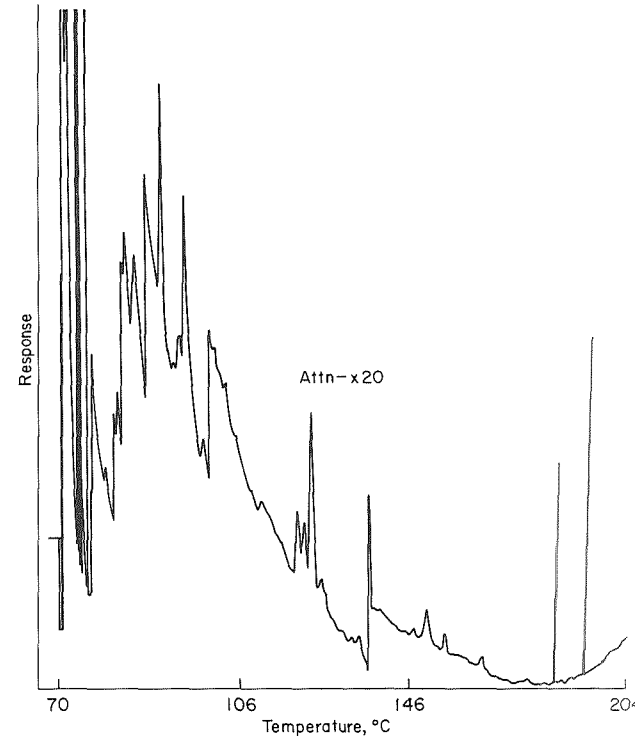


Figure 54 Gas chromatogram of derivatized 1N HCl hydrolysate of trap A from rocket exhaust experiment. Chromatographic conditions as on figure 50(a).

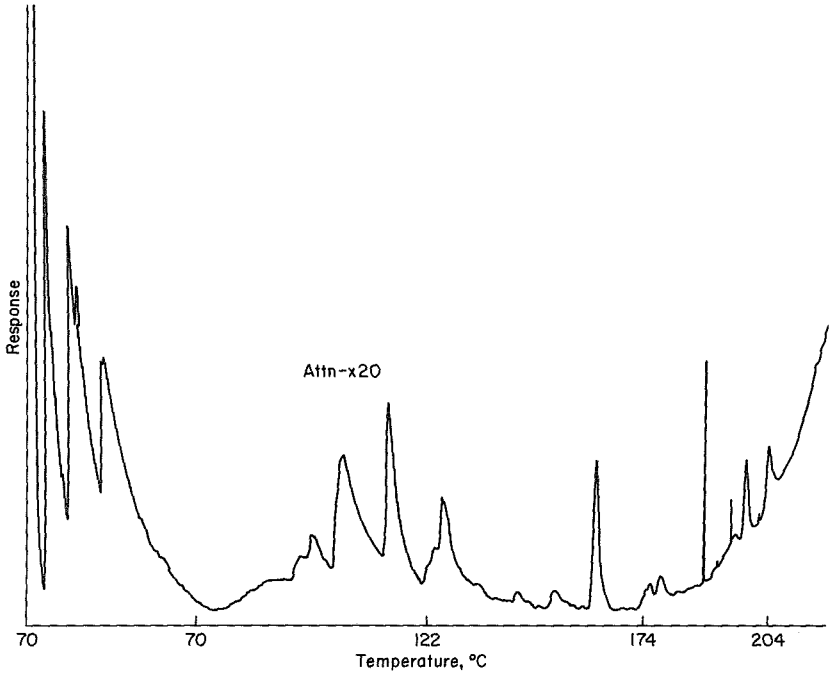


(a) Derivatized 1N HCl hydrolysate of Hawaiian basalt. Chromatographic conditions as on figure 53(a).

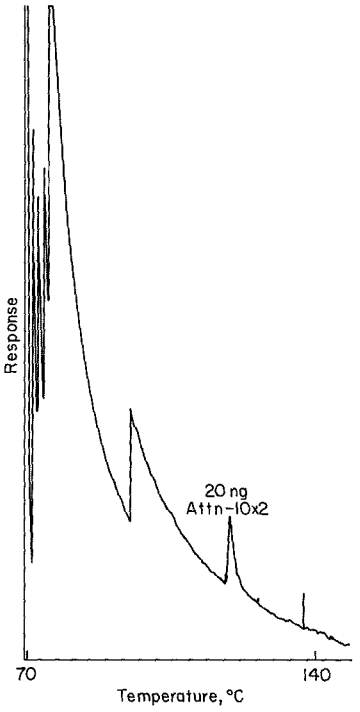


(b) Derivatized pentane extract of 1N HCl hydrolysate of Hawaiian basalt. Chromatographic conditions as on figure 49(a).

Figure 55 Gas chromatograms.



(c) Derivatized 6N HCl hydrolysate of pulverized quartz crystals from Southwest Africa. Chromatographic conditions as on figure 53(a).



(d) Sensitivity check, 2.0 ng of isoleucine. Chromatographic conditions as on figure 49(a).

Figure 55 Concluded

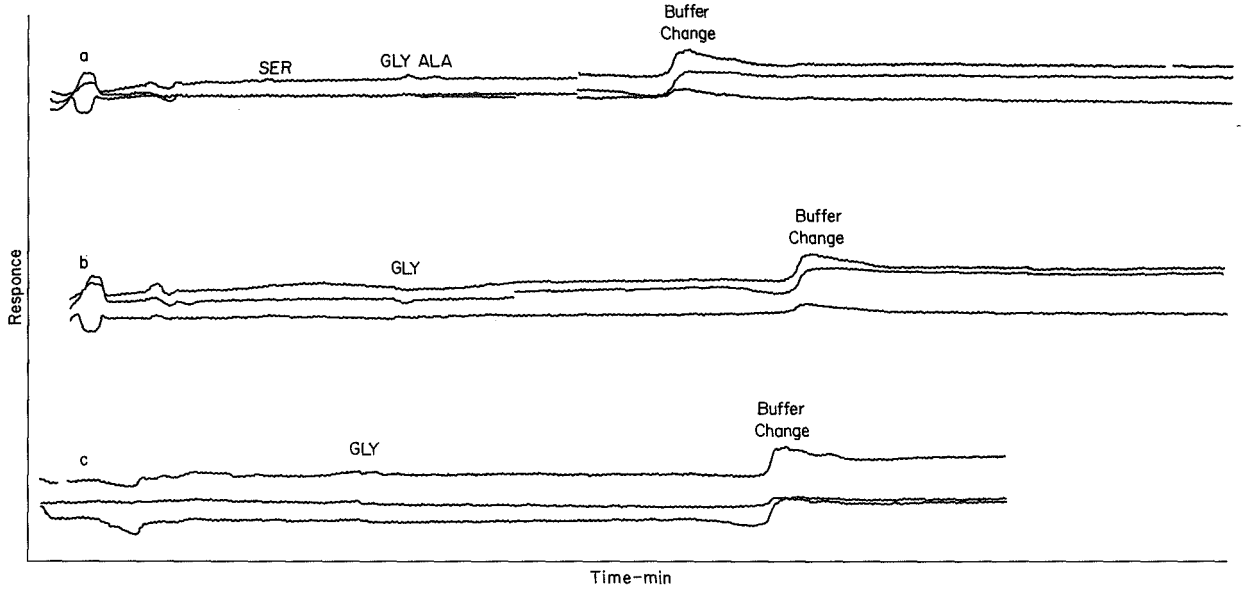
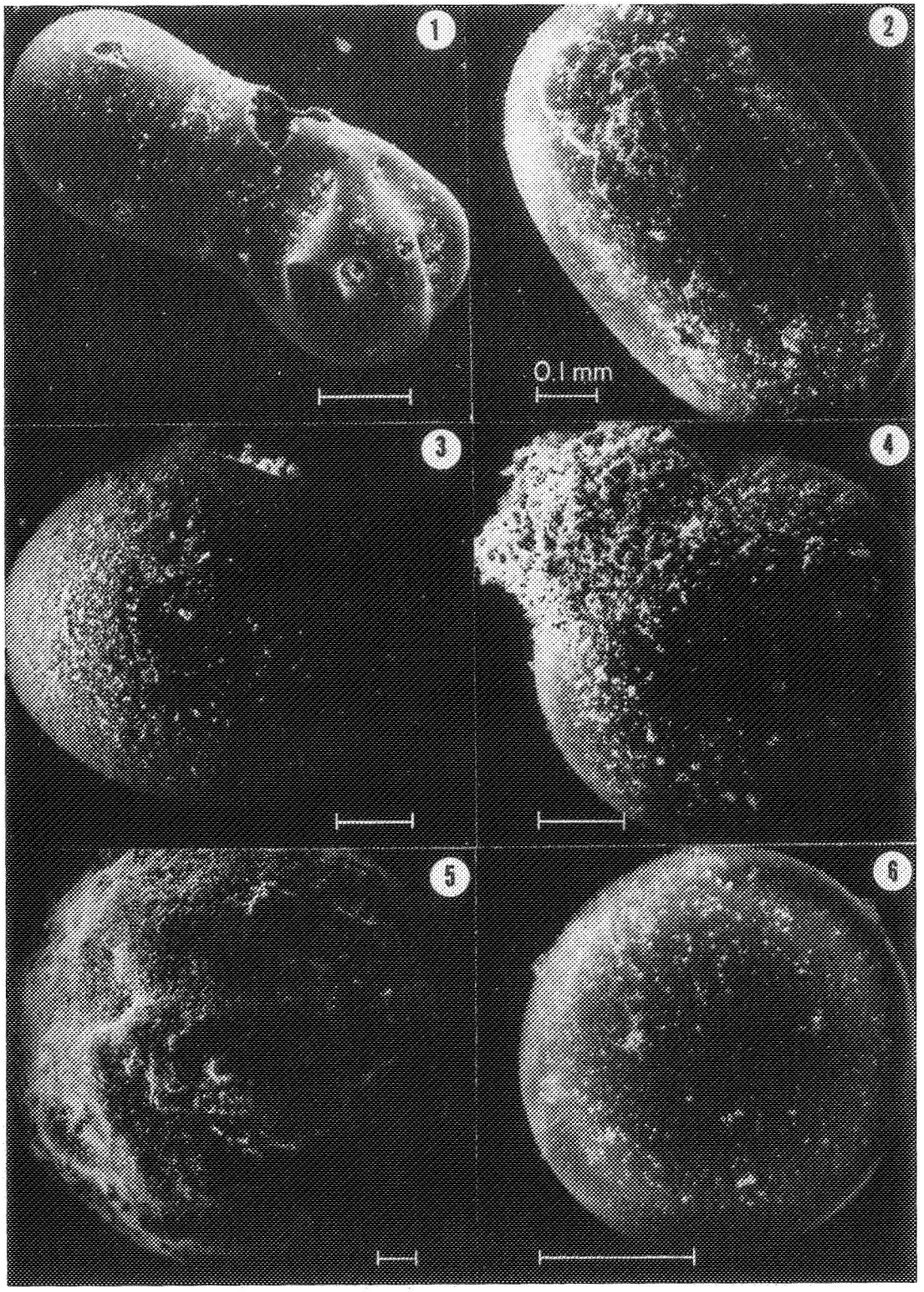


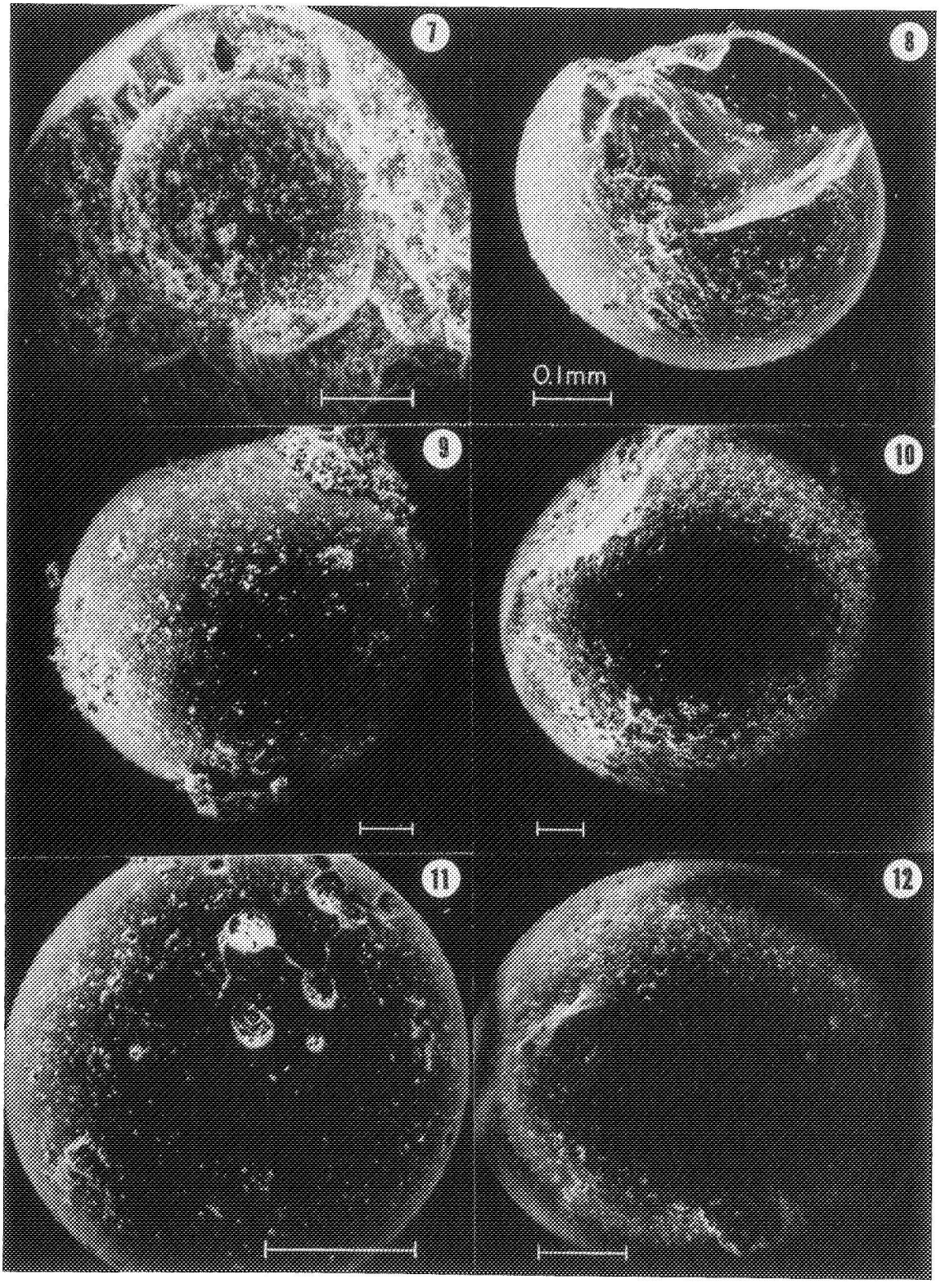
Figure 56 Amino acid analyzer chromatograms. (a) 6N HCl hydrolysate from 1 g of lunar sample. (b) 6N HCl hydrolysate from 1 g of lunar sample, rerun. (c) 6N HCl hydrolysate from 5 g of sand blank.

DESCRIPTION OF PLATES

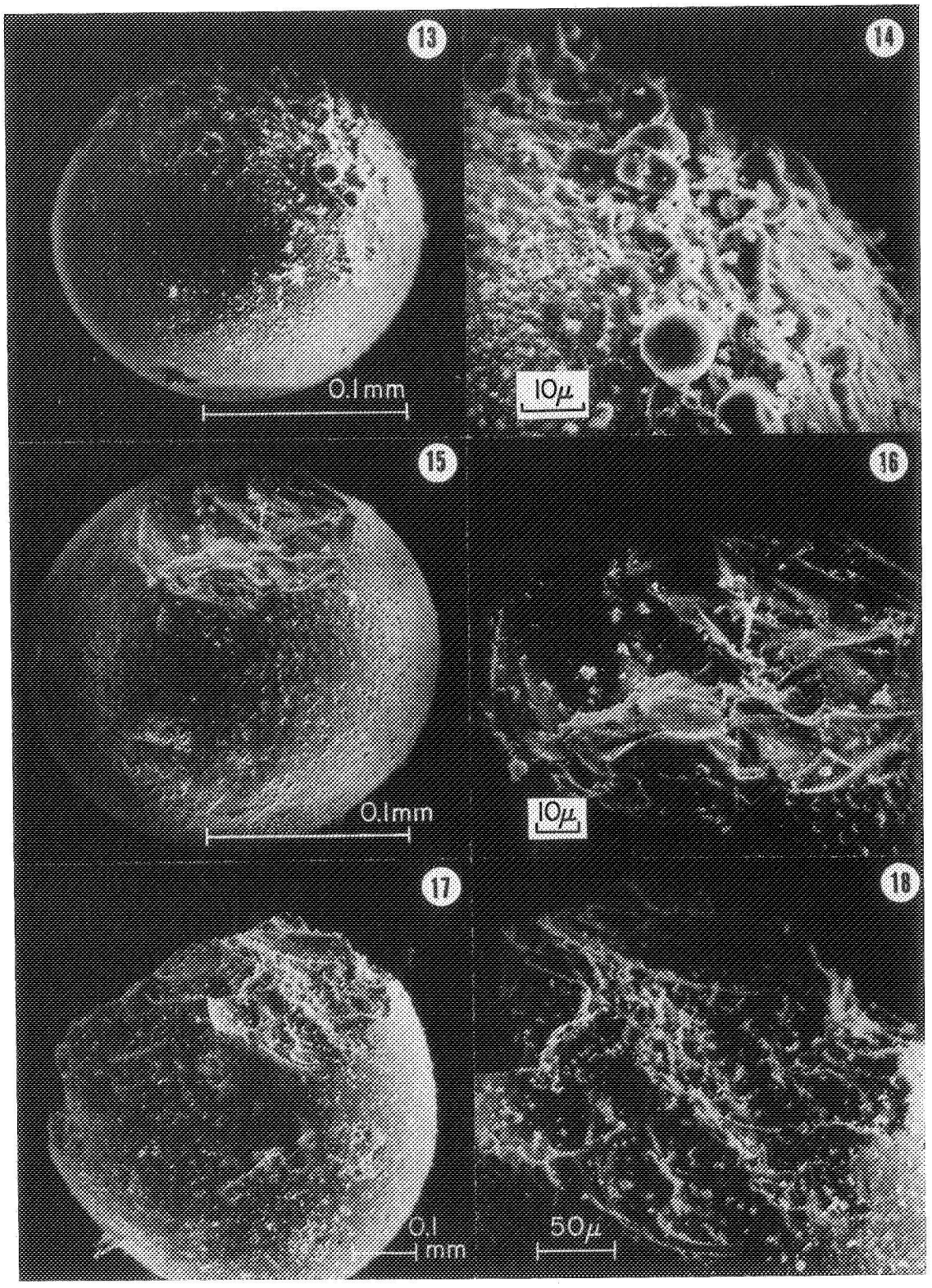
Scanning electron micrographs (Plates 1–32) showing shaped glassy particles (Plates 1–28), filamentous organic contaminants (Plates 29, 30), and rock fragments (Plates 31, 32) in lunar dust from the bulk sample box (Sample 10086,18), and optical photomicrographs (Plates 33–44) showing mineralogic features of petrographic thin sections of microbreccias. Lines for scale in Plates 1–12 represent 0.1 mm; lines for scale in Plates 19–24 represent 10μ.



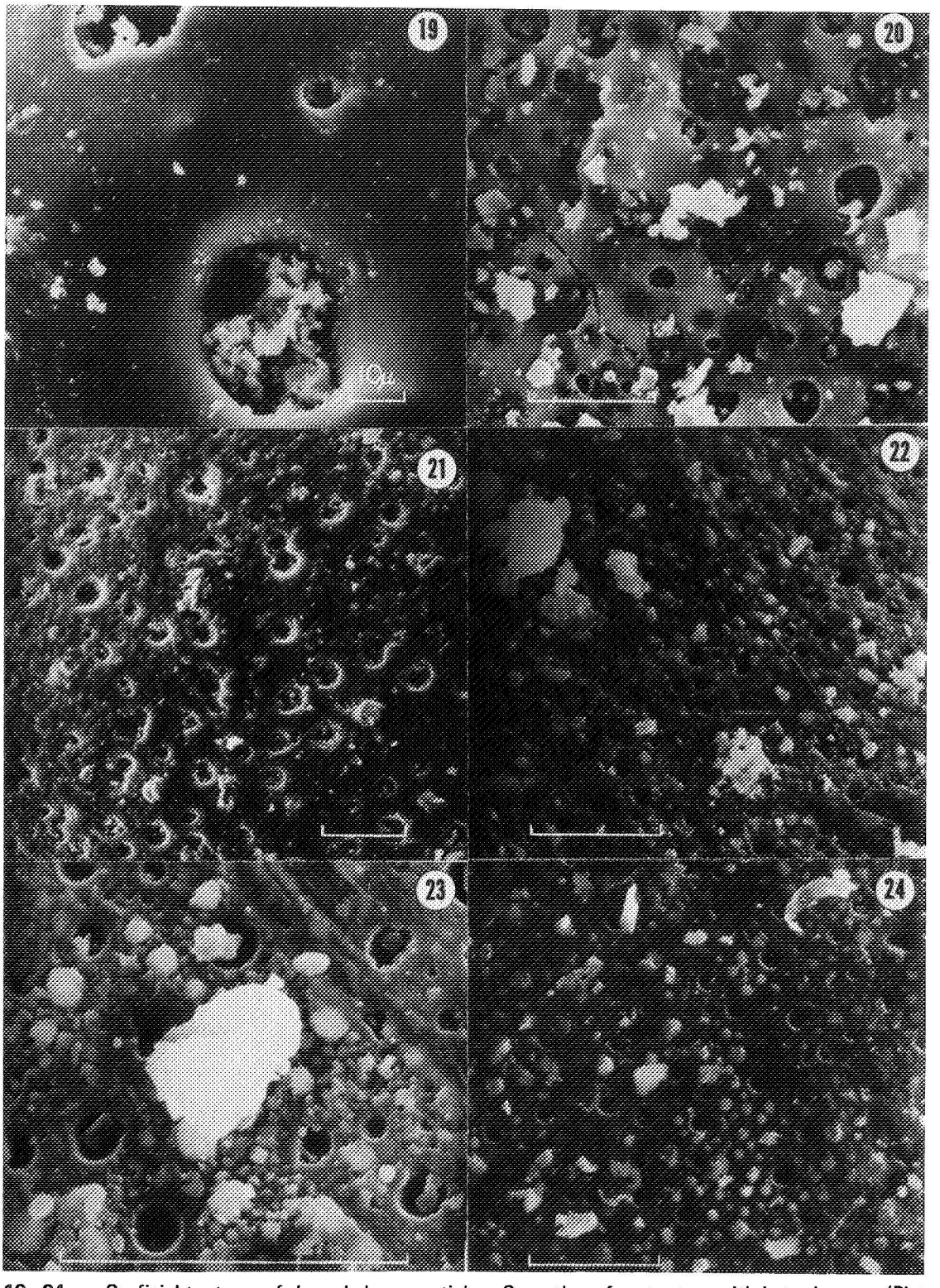
Plates 1–6 Shaped glassy particles. Note the occurrence of equatorial flanges (Plates 2–6), a particulate sintered appendage (Plate 4), and irregular surficial layering (Plate 5).



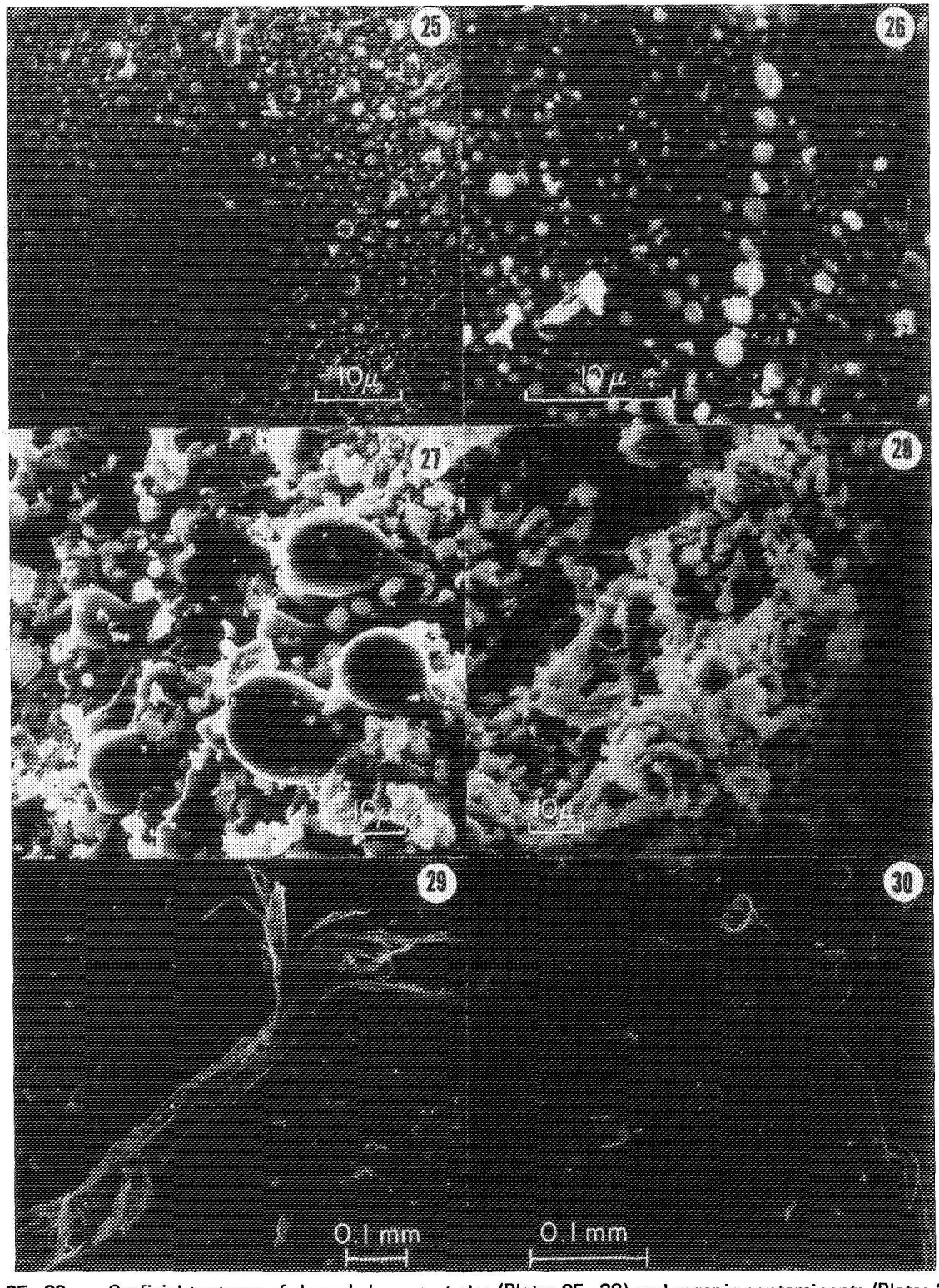
Plates 7–12 Shaped glassy particles. Note the occurrence of both hollow (Plate 7) and solid (Plate 8) spheroids, and the presence of equatorial flanges (Plates 10, 12).



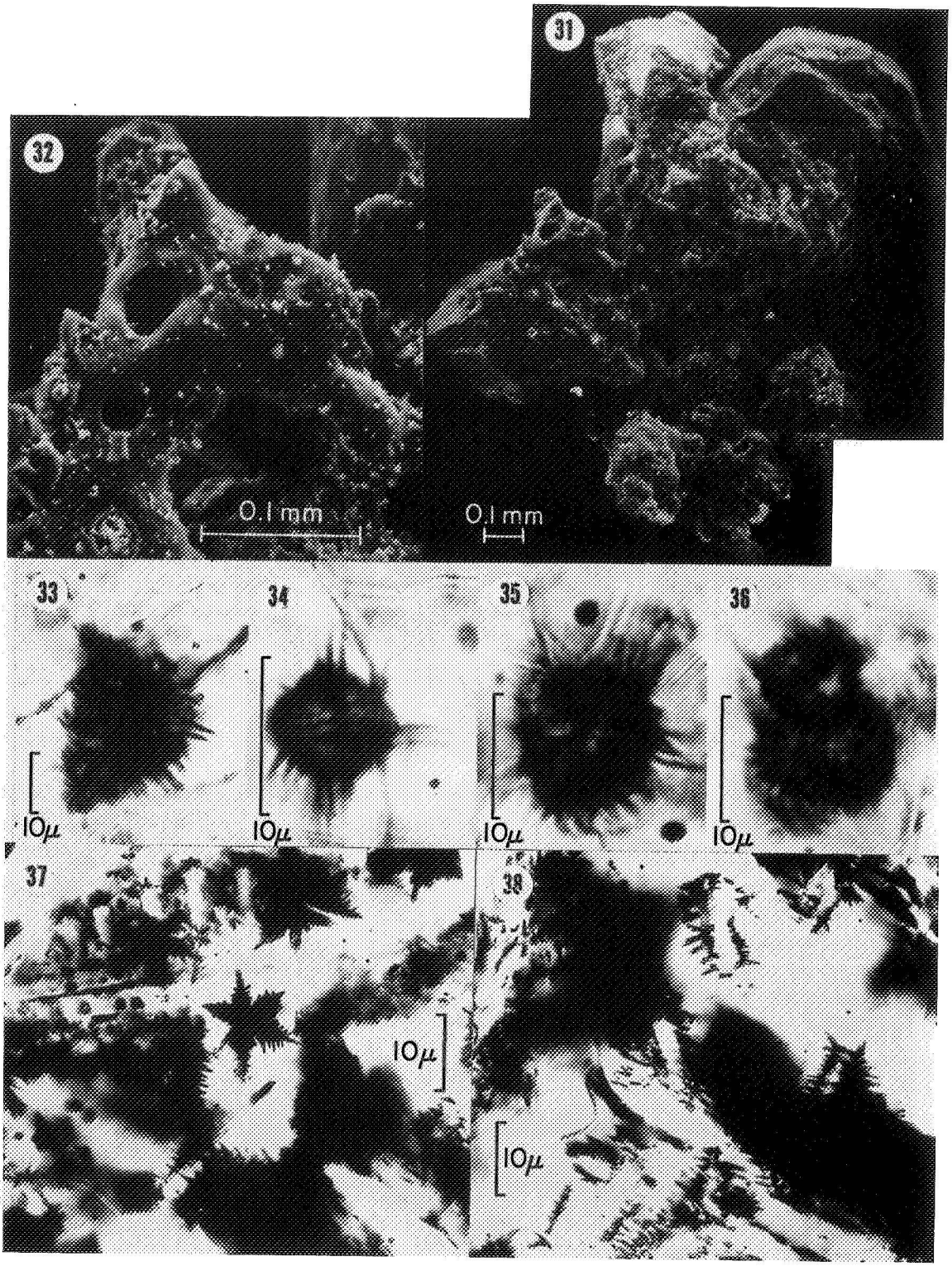
Plates 13–18 Shaped glassy particles. Glass spheroid (Plate 13) with surficial hemispherical papillae (Plate 14); dimpled spheroid (Plate 15) with a well-defined craterlet at one pole (Plate 16); abraded spheroid exhibiting conchoidal fracture (Plates 17, 18).



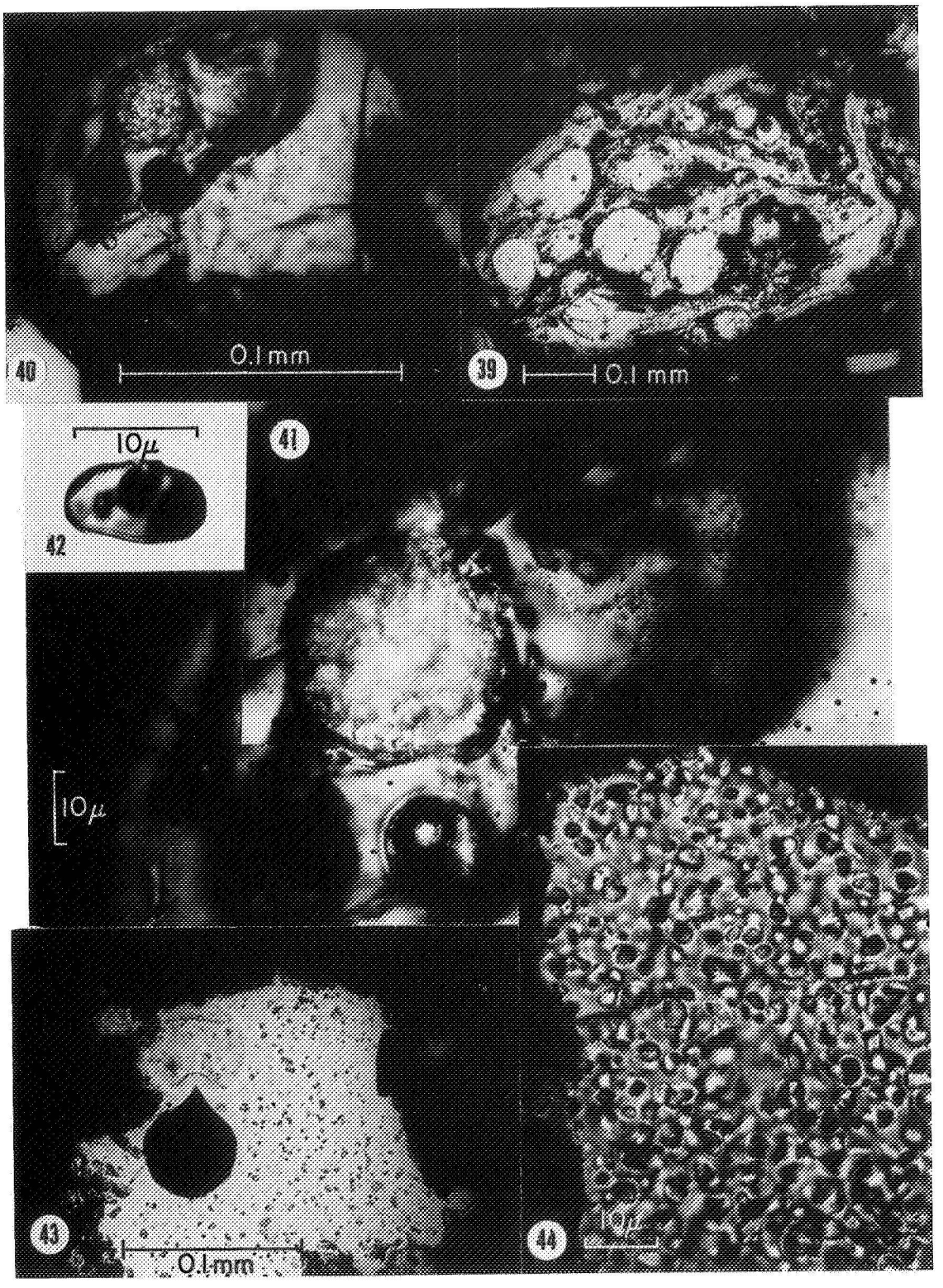
Plates 19–24 Surficial textures of shaped glassy particles. Smooth surface texture with irregular vugs (Plate 19) of rod-shaped particle shown in Plate 1; vesicular surface texture (Plate 20) of spheroid shown in Plate 10; pitted surface texture (Plate 21) of spheroid shown in Plates 15 and 16; dimpled surface texture with few papillae (Plates 22, 23); dimpled and papillose surface texture (Plate 24) of spheroid shown in Plate 9.



Plates 25–30 Surficial textures of shaped glassy particles (Plates 25–28) and organic contaminants (Plates 29, 30). Papillose surface texture (Plate 25) of spheroid shown in Plates 13 and 14; chain of papillae (Plate 26) on surface of ellipsoid shown in Plate 3; large surficial papillae (Plate 27); irregularly vesicular interior portion of an abraded spheroid (Plate 28); shreddy plant fragment (Plate 29); twisted thread-like contaminant (Plate 30).



Plates 31–38 Glassy rock fragment (Plates 31, 32), globular, actinomorphic pseudofossils (Plates 33–36, thin section 10046,56) and devitrification structures (Plates 37, 38, thin section 10059,32).



Plates 39–44 Complex glass ellipsoids (Plate 39, thin section 10061,27; plates 40, 41, thin section 10059,32), rod-shaped glass particle (Plate 42, thin section 10019,15), grinding abrasive extruded from bubble in mounting medium (Plate 43, thin section 10046,56), and mineral inclusions in glassy matrix (Plate 44, thin section 10019,15).

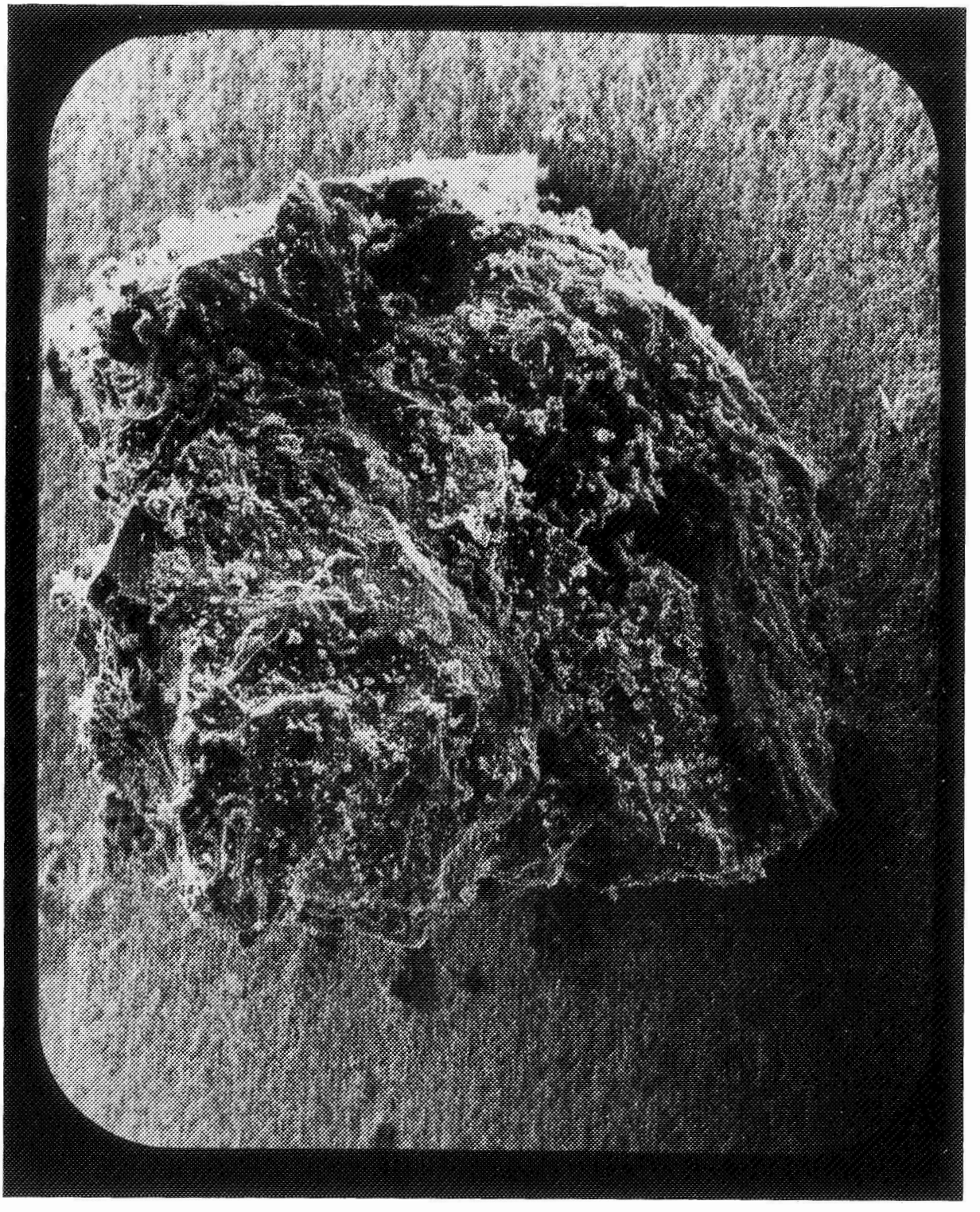


Plate 45 Sharp angular fragments, ×320.

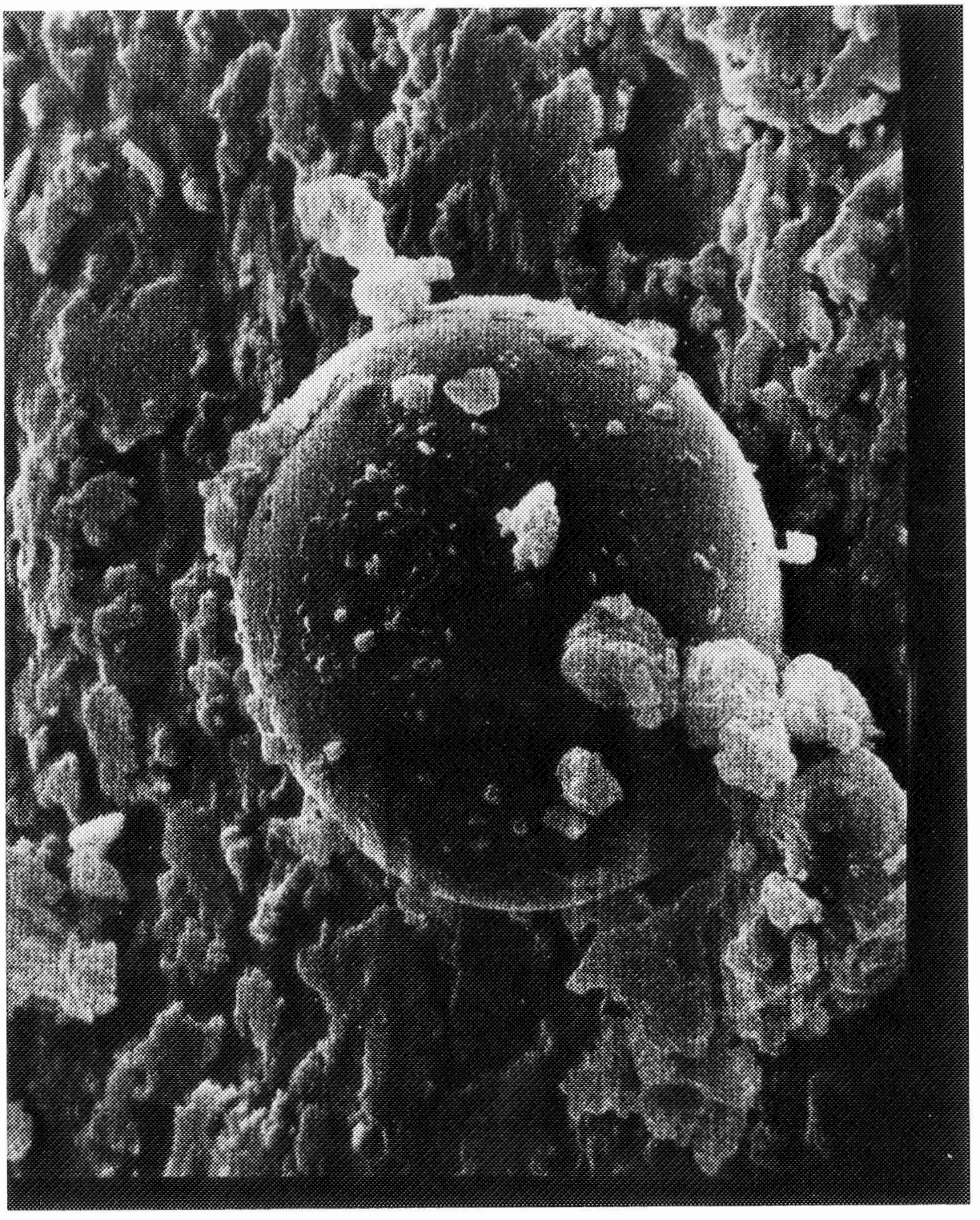


Plate 46 Glassy sphere, X6700.

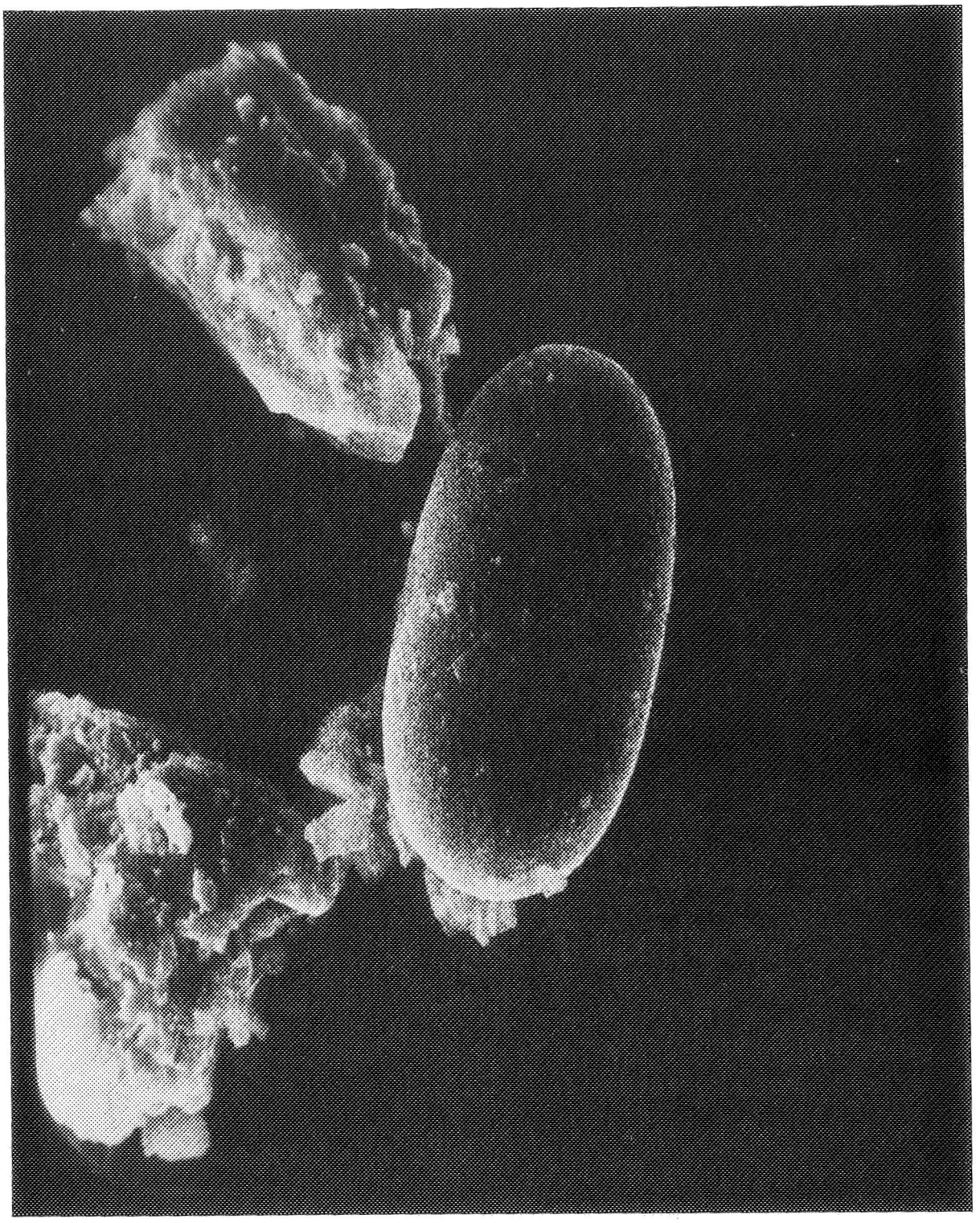


Plate 47 Globular body, ×3200.

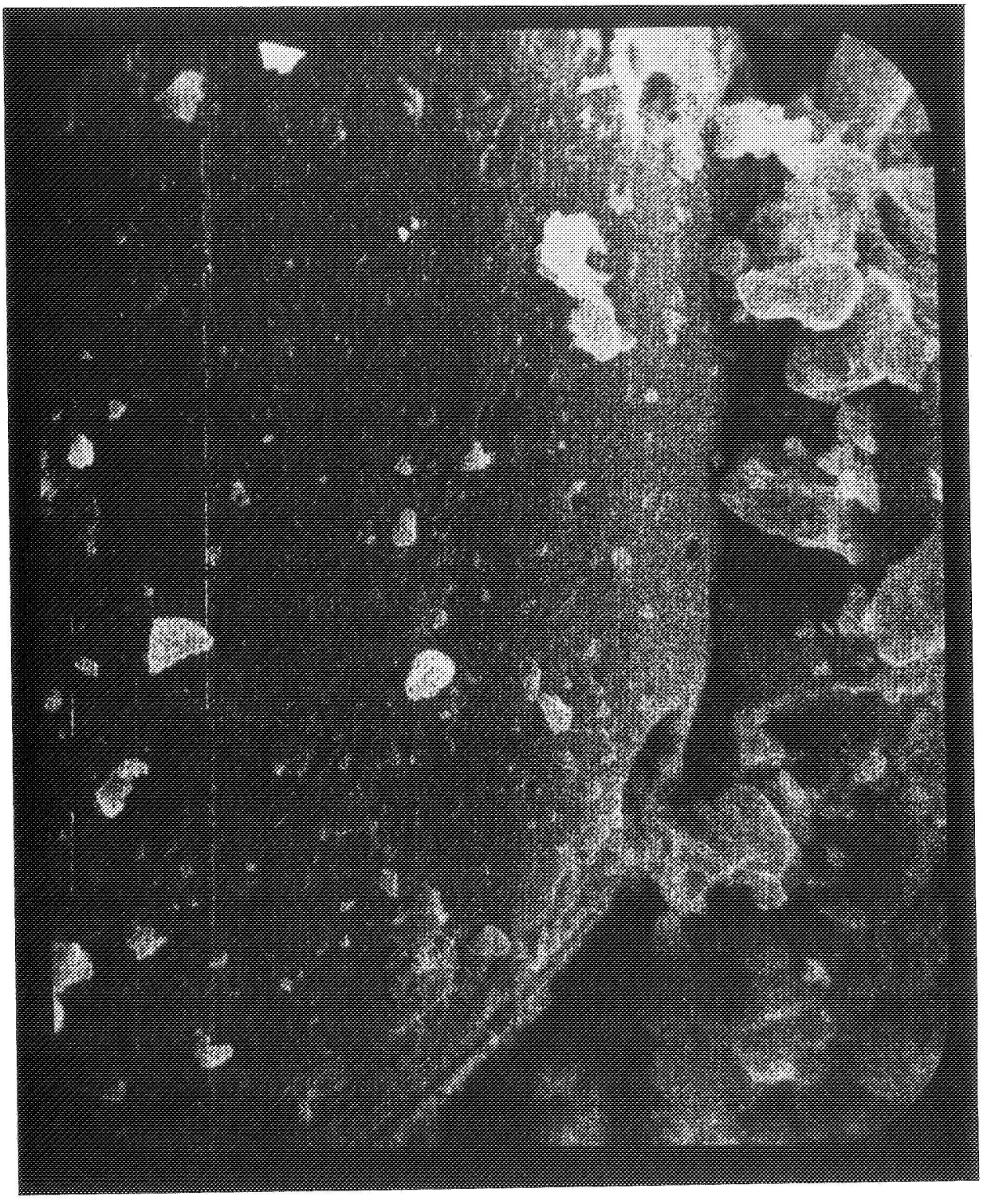


Plate 48 Pores in spheres, X5100.

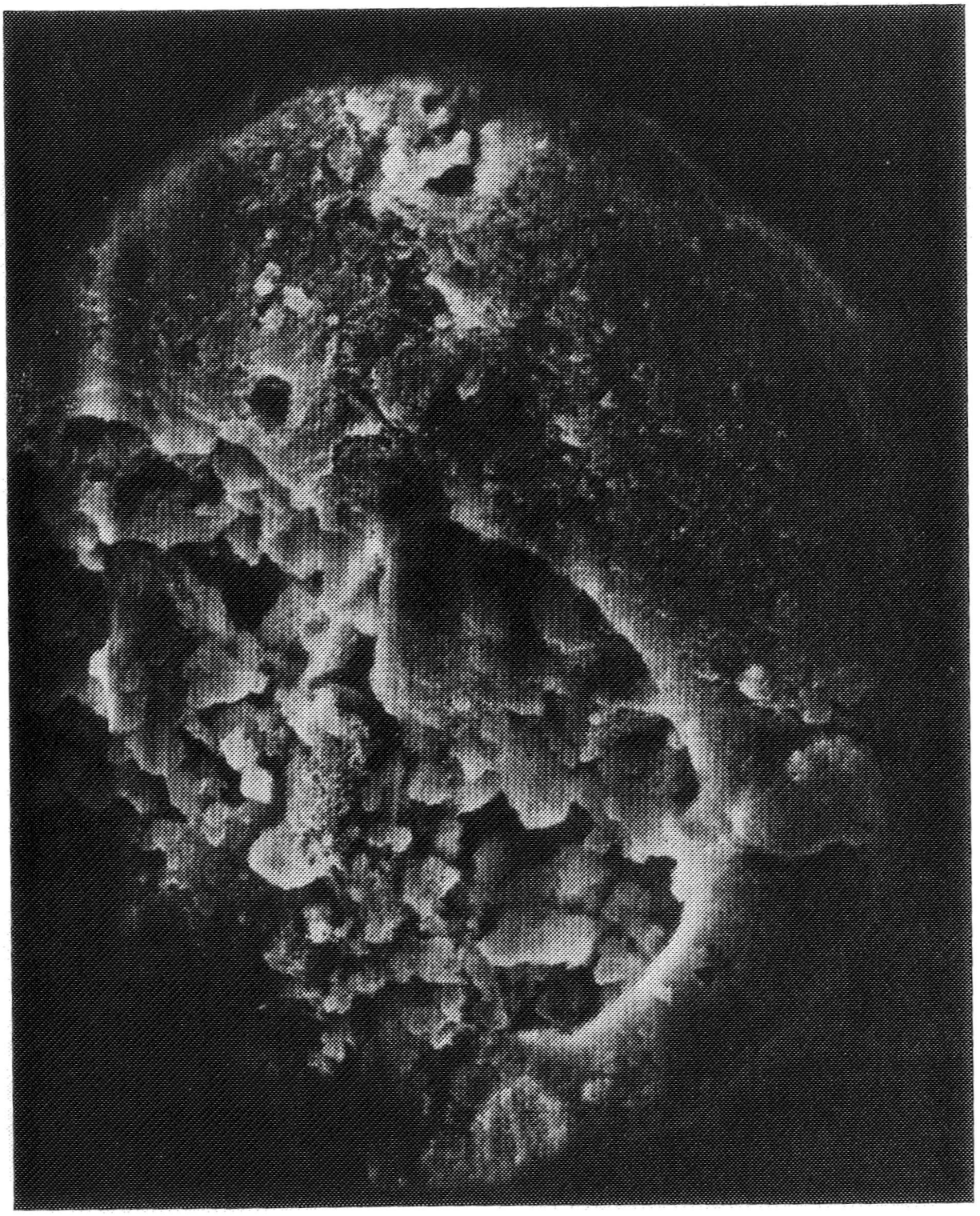


Plate 49 Glass sphere with fines embedded, X3360.

NASA-Langley, 1971 —— 30 A-3669

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